Stille Cross-Coupling of a Racemic Planar-Chiral Ferrocene and Crystallographic Trace Analysis of Catalysis Intermediates and By-products

by **Immo Weber***[1]), **Frank W. Heinemann**, **Panagiotis Bakatselos**, and **Ulrich Zenneck**

Institut für Anorganische Chemie, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstrasse 1, D-91058 Erlangen

Dedicated to the memory of Professor *John K. Stille* Ph.D.

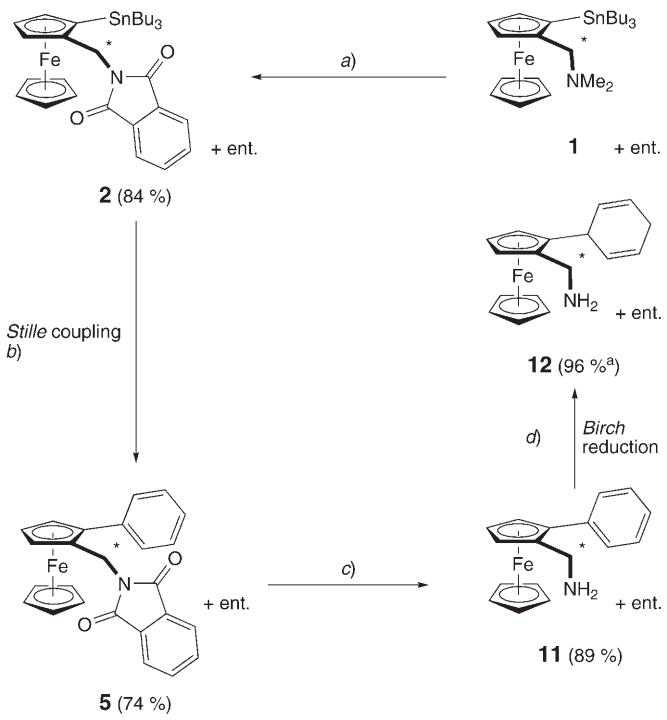
A pressure-controlled procedure for the S_N1 reaction of *rac*-1-[(dimethylamino)methyl]-2-(tributylstannyl)ferrocene (**1**) to *rac*-1-(phthalimidomethyl)-2-(tributylstannyl)ferrocene (**2**) was developed. Pd^0-Catalyzed *Stille* coupling of **2** with iodobenzene afforded *rac*-1-phenyl-2-(*N*-phthalimidomethyl)-ferrocene (**5**) in 74% yield; after trace enrichment by crystallization of the combined mother liquors, one single crystal of each, **5**, catalysis intermediate *trans*-iodo(*σ*-phenyl)bis(triphenylarsino)palladium(II) (**7**), *trans*-diiodobis(triphenylarsino)palladium(II) (**8**), and *rac*-2,2′-bis(phthalimidomethyl)-1,1′-biferrocene (**9**) could be isolated by crystal sorting under a microscope and characterized by X-ray crystal structure analysis. Furthermore, **5** was deprotected to amine (**11**), which does even survive the *Birch* reduction to *rac*-1-(aminomethyl)-2-(cyclohexa-2,5-dienyl)ferrocene (**12**).

1. Introduction. – Because of their unique properties, 1,2-disubstituted planar-chiral ferrocenyl ligands gained a fundamental role in enantioselective catalysis over the past decade [1a–h]. Mostly established by *Togni* and co-workers [1a–f], planar-chiral 1,2-disubstituted ferrocenes are obtained in two steps starting from a ferrocene template bearing a chiral auxiliary group, such as *Ugi*'s (*R*)- or (*S*)-[1-(dimethylamino)ethyl]-ferrocene [1i]: The first ligating functionality is introduced *via* diastereoselective *ortho* lithiation followed by electrophile quenching, the second by nucleophilic substitution of the dimethylamino group. Enantioselective Pd^0-catalyzed transformations [2a] are of vast synthetic utility. *Pedersen*'s monodentate planar-chiral ferrocene ligands proved to be highly active and enantioselective for Pd^0-catalyzed hydrosilylation reactions [2b,c], which contain an arene in *ortho* position to the donor group. Generally, coupling of arene units with ferrocene cores have been achieved *via* Pd^0-catalyzed *Negishi* [2b–e] and *Stille* [3] cross-coupling reactions. Air-stable planar-chiral *ortho*-(tributylstannyl)-ferrocenes are very attractive intermediates due to their synthetic versatility. Besides *Stille* couplings with various aryl iodides, the stannyl group can be exchanged with BuLi followed by quenching with electrophiles; direct halo exchange in the sense of an 'Umpolung' for coupling reactions is also possible [3b]. For catalytic applications, we became also interested in planar-chiral *ortho*-substituted arylferrocene derivatives [4]. In a preliminary study, starting from *rac*-1-[(dimethylamino)methyl]-2-(tributylstan-

[1]) Present address: *Kunststoff- und Metallwaren-Fabrik* (*KUM*) *GmbH & Co. KG*, Abteilung Forschung und Entwicklung, Essenbacher Strasse 2, D-91054 Erlangen (phone: ++49-(0)9131-826823; fax: ++49-(0)9131-788629; e-mail: immo.weber@kum.net).

nyl)ferrocene (**1**) [3c] (*Scheme 1*), we therefore explored the *Stille* coupling reaction of a racemic planar chiral stannylated ferrocene because protocols reported in [3] vary in detail (ligands, additives, solvents, temperature).

Scheme 1

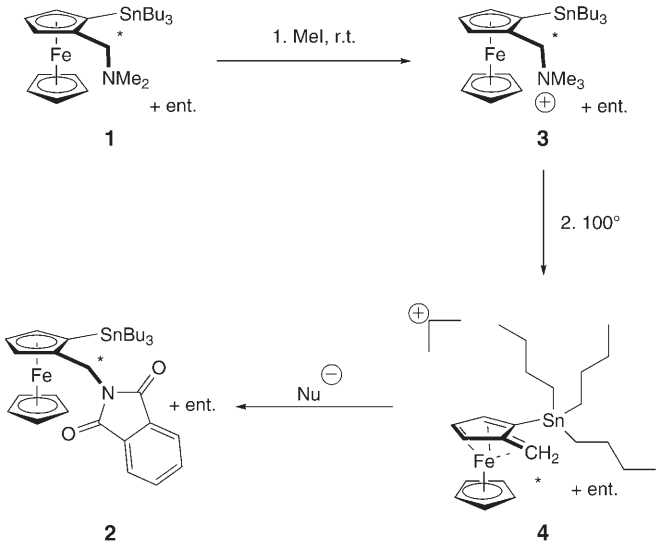


a) In closed *Schlenk* tube *in situ:* 1. MeI (1.1 equiv.), DMF r.t.; 2. Et_3N (0.4 equiv.), r.t.; 3. potassium phthalimide (1.4 equiv.), 100°, 15 h. *b*) Catalyst mixture $[Pd_2(dba)_3]\cdot CHCl_3$ (0.025 equiv.)/$AsPh_3$ (0.15 equiv.)/CuI (0.50 equiv.) PhI (1.9 equiv.), DMF, 70°, 14 h. *c*) Hydrazine hydrate (10.4 equiv.), EtOH, 70°, 1 h. *d*) Li (12.5 equiv.)/liq. ammonia, EtOH, THF, −78°; 2. NH_4Cl (13.8 equiv.).

[a]) Product not further purified.

2. Results and Discussion. – For the nucleophilic substitution reaction of the dimethylamino group of **1** with potassium phthalimide to *rac*-1-(phthalimidomethyl)-2-(tributylstannyl)ferrocene (**2**), *Weissensteiner*'s protocol [5a,b] was envisaged (*Scheme 2*). A dialkylamino group of an 1,2-disubstituted planar-chiral ferrocene derivative such as **1** is activated by permethylation and then substituted with nucleophiles under reflux in a polar aprotic solvent (DMF, MeCN, *etc.*) in S_N1 fashion, which is well established to proceed *via* ($\eta^4:\eta^2$)-fulvenium complexes [1a–c][1e,f]. Such complexes were isolated [5c]. However, this method is not easily applicable for ferrocene derivatives with highly activating electron-donor substituents such as trialkylstannyl groups, which are bulky at the same time. In the case here, the corresponding energetically stabilized ($\eta^4:\eta^2$)-fulvenium complex (**4**) (*Scheme 2*) is

Scheme 2. *in situ* S_N1*-Type Reaction Pathway of* **1** *to* **2** via *(*$\eta^4:\eta^2$*)-Fulvenium Intermediate* **4**

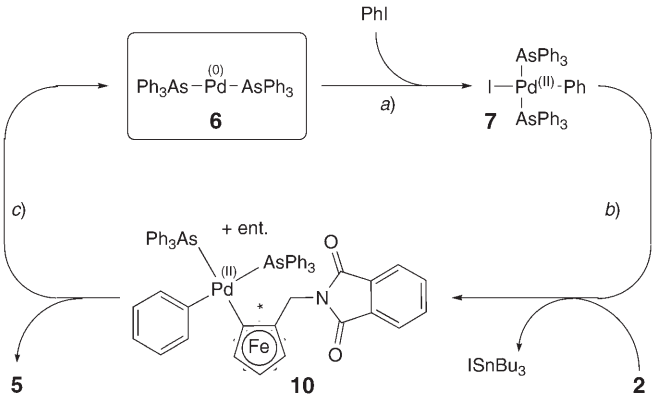


a) Oxidative addition of iodobenzene to catalyst **6** (see *Scheme 3*). *b*) Transmetallation (often rate limiting). *c*) Reductive elimination to coupling product **5** and backformation of **6**.

readily formed from **3** under the extrusion of Me_3N, but decomposes also faster than the subsequent reaction with the nucleophile can occur, due to steric repulsion. Therefore, these two antagonistic effects cannot be overcome by simple temperature control. To outflank this dilemma, the *Weissensteiner* protocol was optimized to an *in situ* and pressure-controlled procedure for the synthesis of *rac*-ferrocene derivative **2**. Ferrocene derivative **1** was directly *N*-permethylated in DMF with MeI ($\rightarrow$ **3**), followed by addition of potassium phthalimide and heating in a closed *Schlenk* tube. Keeping the mixture under pressure in this way decelerates the formation of the ($\eta^4:\eta^2$)-fulvenium complex **4** sufficiently to give the potassium phthalimide enough time to react since gaseous Et_3N cannot escape the closed system. Choosing DMF as solvent has the advantage that **2** is constantly removed because it separates as a second and less polar liquid phase. With this method, racemic **2** was obtained in 84% yield after purification. Quenching of excess MeI with Et_3N after *N*-permethylation is essential. Otherwise *N*-methylphthalimide forms which cannot be easily removed from the desired reaction product leading to significant losses in yield.

The *Stille* cross-coupling of **2** with iodobenzene to *rac*-1-phenyl-2-(phthalimidomethyl)ferrocene (**5**) was oriented on *Curnow*'s procedure [6a] for coupling electron-rich and sterically demanding stannyl compounds with iodobenzene. A mixture of 5 mol-% Pd^0 from 2.5 mol-% $[Pd_2(dba)_3]\cdot CHCl_3$/CuI/$AsPh_3$ 1:10:3 (dba = dibenzylideneacetone = 1.5-diphenylpenta-1,4-dien-3-one) in DMF was also found to be optimal here. The actual catalyst formed *in situ* is obviously bis(triphenylarsino)-palladium(0) (**6**) (see *Scheme 3* for a generally accepted catalytic cycle proposed on coupling of **2** to **5**). After recrystallization, racemic **5** was obtained in 74% yield.

Scheme 3. *Catalytic Cycle Proposed for the* Stille *Coupling of* **2** *to* **5**



Unfortunately, traces of other by-products could not be removed completely from **5**, also not by column chromatography, so a correct elementary analysis could not be obtained. Crystallization of combined mother liquors succeeded at least in a trace enrichment of these impurities, *i.e.*, of **7**–**9** (*Scheme 3*). Single crystals of racemic **5** (*Fig. 1*, *Table 1*)[2]), catalysis intermediate (**7**) (*Fig. 2*, *Table 2*), diiodo complex (**8**) (*Fig. 3*, *Table 3*) and of *rac*-2,2′-bis(phthalimidomethyl)-1,1′-biferrocene (**9**; *Fig. 4*, *Table 4*) were obtained 'à la *Pasteur*' by tedious sorting under a microscope[3]).

The catalysis intermediate **7** is isostructural to the analog phosphine complex *trans*-[$Pd^{II}(I)(Ph)(PPh_3)_2$] in the solid state, but not isomorphous [6b]. Intermediate **7** shows furthermore an extraordinary *trans* influence of the σ-phenyl on the iodo ligand because nearly all ligands are bent out of the square planar geometry compared with the nearly perfect square planar structure of diiodo complex **8**. Three possible explanations for the formation of the racemic *like-like* ferrocene diastereoisomer **9**,

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[2]) Coupling product **5** crystallized so fast, even under slow solvent diffusion into a diluted solution, that suitable crystals for X-ray structure analysis could be only obtained by slow crystallization from the combined mother liquors.

[3]) After solvent removal, the combined mother liquors contained nearly exclusively iodobenzene and **5**; in the NMR spectra of the crude product and of the combined mother liquors, Pd^{II} complexes **7** and **8** as well as by-product **9** could be only insufficiently identified due to signal overlap and very low concentration (δ 7–8, aromatic region, δ 4–6, η^5-cyclopentadienyl moieties). A full spectroscopic analysis of **7**–**9** was not possible due to the low amount of material isolated.

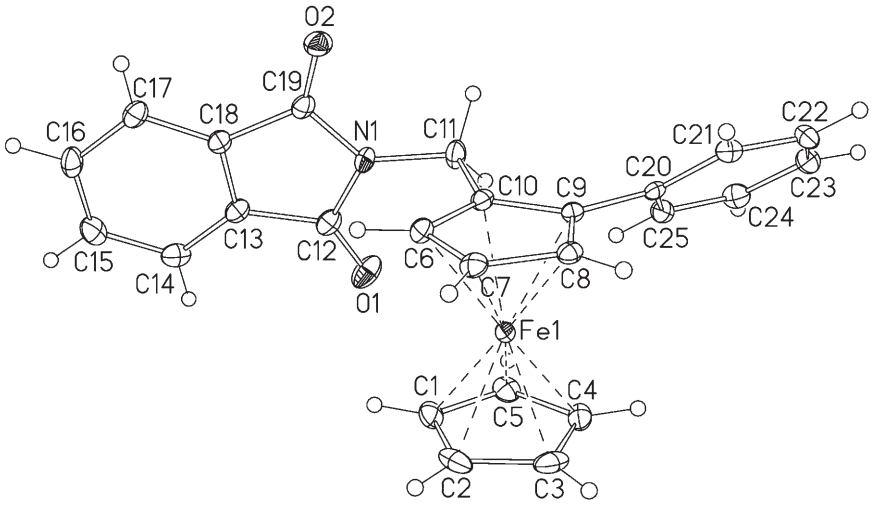

Fig. 1. *Thermal ellipsoid plot* (50% probality) *of racemic* **5**. The (*P*)-enantiomer is shown; for selected bond distances and angles, see *Table 1*.

Table 1. *Selected Bond Distances and Bond Angles of* rac-**5**

Distance	[Å]	Bond angle	[°]
N(1)–C(11)	1.458(2)	N(1)–C(11)–C(10)	111.2(2)
C(11)–C(10)	1.513(2)	C(11)–C(10)–C(9)	126.7(2)
C(10)–C(9)	1.441(2)	C(10)–C(9)–C(20)	128.6(2)
C(9)–C(20)	1.486(2)	C(9)–Fe(1)–C(1)	149.28(7)
C(9)–Fe(1)	2.053(2)	C(9)–Fe(1)–C(2)	169.08(7)
C(10)–Fe(1)	2.047(2)	C(10)–Fe(1)–C(2)	148.77(7)
		C(10)–Fe(1)–C(3)	169.26(7)

which bears two chiral planes and one chiral axis, can be given: *i*) intramolecular *ipso* transmetallation of Pd^{II} intermediate **10** (*Scheme 3*) followed by reductive elimination to catalyst **6** and by-product **9**; *ii*) transmetallation of two molecules **2** on a $[Pd^{II}(AsPh_3)_2]$ complex similar to **8** evolved from oxidation followed again by reductive elimination to **6** and **9**; *iii*) or most likely, the formation of **9** is due to transmetallation of two molecules **2** on traces of Cu^{II} resulting then in an *Ullmann*-type reductive elimination [6c–e].

Complementary, it should be mentioned that the synthesis of 2,2′-diformyl-1,1′-biferrocene *via Ullmann* coupling has been achieved by *Nicolosi* and co-workers [6e]. The last explanation (*iii*)) is also consistent with the fact that copper salts are often required for *Stille* cross-coupling reactions which do not proceed otherwise. In this sense, CuI or CuO might activate the Sn–C bond enabling transmetallation. Furthermore, simple alkynes couple with iodoferrocenes just in the presence of copper salts by using a palladium catalyst [6f]. Copper salts could also trap excess ligand, but this is of debate because copper salts have to be added stoichiometrically also to *Stille* coupling reactions with preformed Pd^0 catalysts containing bidentate ligands [3b]. In

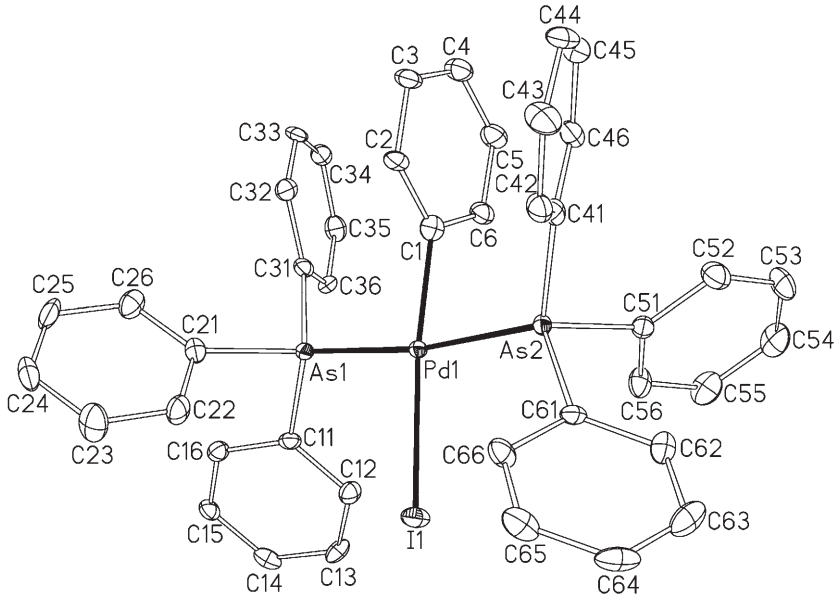

Fig. 2. *Thermal ellipsoid plot* (50% probality) *of catalysis intermediate* trans-*[Pd^{II}(I)(Ph)(AsPh$_3$)$_2$]* (**7**). H-Atoms are omitted for clarity; for selected bond distances and angles, see *Table 2*.

Table 2. *Selected Bond Distances and Bond Angles of Catalysis Intermediate* trans-*[Pd^{II}(I)(Ph)(AsPh$_3$)$_2$]* (**7**)

Distance	[Å]	Bond angle	[°]
Pd(1)–As(1)	2.4335(6)	As(1)–Pd(1)–As(2)	171.77(2)
Pd(1)–As(2)	2.4187(6)	C(1)–Pd(1)–I(1)	173.5(2)
Pd(1)–I(1)	2.6743(7)	C(1)–Pd(1)–As(2)	83.9(2)
Pd(1)–C(1)	2.010(5)	I(1)–Pd(1)–As(1)	94.47(2)

our hands, using triphenylphosphine or 1,1′-bis(diphenylphosphino)ferrocene (dppf) instead of triphenylarsine under otherwise identical reaction conditions did not lead to any success here. All attempts to couple 1-iodo-2-(phthalimidomethyl)ferrocene with stannyl building blocks under otherwise identical reaction conditions (5 mol-% Pd^0/CuI/$AsPh_3$ 1:10:3 in DMF) failed as well.

Racemic ferrocene **5** was then deprotected with hydrazine to the free primary amine **11** in 89% yield after chromatography (*Scheme 1*). *Birch* reduction [7] of **11** required *ca.* 12.5 equiv. of lithium. THF had to be used as a cosolvent due to the low solubility of **11** in EtOH at low temperature. Nevertheless, cyclohexadienylferrocene **12** was obtained nearly pure in 96% yield without further purification. The ferrocene backbone stayed intact during the *Birch* reduction. However, all attempts to induce **12** to react with $RuCl_3$ to the corresponding *ansa* complex *rac*-dichloro{1-[(amino-κN)methyl]-2-(η^6-phenyl)ferrocene}ruthenium(II) under standard conditions (ammonium salt, EtOH) [8] resulted in total decomposition. It was also tried to let **12** react

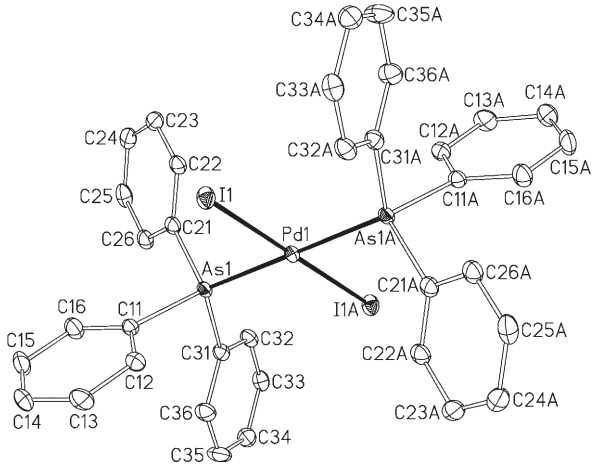

Fig. 3. *Thermal ellipsoid plot* (50% probality) *of* trans-*[$Pd^{II}(I)_2(AsPh_3)_2$]* (**8**). H-Atoms are omitted for clarity; for selected bond distances and angles, see *Table 3*.

Table 3. *Selected Bond Distances and Bond Angles of* trans-*[$Pd^{II}(I)_2(AsPh_3)_2$]* (**8**)

Distance	[Å]	Bond angle	[°]
Pd(1)–As(1)	2.4356(3)	As(1)–Pd(1)–As(1A)[a])	180
Pd(1)–I(1)	2.6060(3)	I(1)–Pd(1)–I(1A)[a])	180
		As(1)–Pd(1)–I(1)	88.04(1)
		I(1)–Pd(1)–As(1A)[a])	91.96(1)

[a]) Symmetry transformation: $-x+1, -y+1, -z$

with 'ruthenium ink' (preformed by refluxing $RuCl_3$ in EtOH), without success. A brief investigation of this 'blue ink' by cyclovoltammetry (CV), which is said to consist only of Ru^{II} ions, a widespread statement in textbooks, revealed that 'ruthenium ink' is a 'living solution' of Ru^{III} species with standard potentials around 700 mV in the sense that this solution dynamically changes in composition without reaching a defined equilibrium. This is well above the standard potential of 450–500 mV typically found for ferrocene derivatives, so the failure of this synthesis attempt is due to the oxidation of the ferrocene moiety by Ru^{III}. Therefore, further attempts to obtain the desired *ansa* complex, even by variation of this method, were abandoned. Conclusively, for the direct synthesis of [Ru^{II}(η^6-arene)] complexes with $RuCl_3$ in alcoholic solution, the substituents attached at the cyclohexadiene derivatives must be capable to withstand an oxidation potential above 700 mV.

3. Conclusions. – Although the originally anticipated synthesis of the *ansa* [Ru^{II}(η^6-arene)] complex had to fail, both, the *in situ* substitution of **1** to **2** and the *Stille* coupling of **2** to **5** are of potential synthetic utility: A detour for the preparation of 1,2-disubstituted planar-chiral ferrocene ligands *via ortho*-stannylated ferrocene analogs of **1** is indicated if the desired *ortho* substituents strongly deactivate the formation of the corresponding ($\eta^4:\eta^2$)-fulvenium complex or if they are prone for side reactions in the

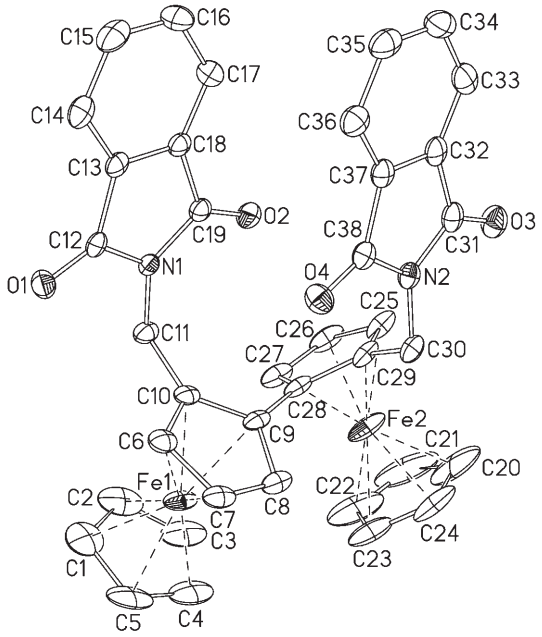

Fig. 4. *Thermal ellipsoid plot* (50% probality) *of* rac-*2,2′-bis(phthalimidomethyl)-1,1′-biferrocene* (**9**). The (*M*,*M*,*M*)-diastereoisomer is shown; H-atoms are omitted for clarity; for selected bond distances and angles, see *Table 4*.

Table 4. *Selected Bond Distances and Bond Angles of* rac-*2,2′-Bis(phthalimidomethyl)-1,1′-biferrocene* (**9**)

Distance	[Å]	Bond angle	[°]
N(1)–C(11)	1.469(3)	N(1)–C(11)–C(10)	113.0(2)
C(11)–C(10)	1.502(4)	C(11)–C(10)–C(9)	126.4(3)
C(10)–C(9)	1.441(4)	C(10)–C(9)–C(28)	125.2(2)
C(9)–C(28)	1.472(4)	C(9)–C(28)–C(29)	125.7(2)
C(28)–C(29)	1.434(4)	C(28)–C(29)–C(30)	126.0(3)
C(29)–C(30)	1.501(4)	C(29)–C(30)–N(2)	112.6(2)
C(30)–N(2)	1.464(3)	C(9)–Fe(1)–C(4)	127.2(2)
C(10)–Fe(1)	2.041(3)	C(9)–Fe(1)–C(5)	164.0(2)
C(9)–Fe(1)	2.056(3)	C(10)–Fe(1)–C(5)	153.1(2)
C(28)–Fe(2)	2.060(3)	C(28)–Fe(2)–C(20)	155.4(2)
C(29)–Fe(2)	2.036(3)	C(29)–Fe(2)–C(22)	166.1(2)

following nucleophilic substitution of the (dimethylamino)group. After nucleophilic substitution at the fulvenic position, the originally desired *ortho* substituent can be introduced *via* stannyl–lithio exchange followed by electrophile quenching or by a *Stille* coupling with a haloarene, for example. Because catalysis intermediate **7** is isostructural to the analog phosphine complex, the reason for the efficiency of the catalyst mixture applied here (5 mol-% Pd^0/CuI/$AsPh_3$ 1:10:3) in DMF might be

simply based upon the obviously inherent stability of catalyst **6** and of catalysis intermediate **7**. It is remarkable that **7** does not only withstand an aqueous workup with an aqueous fluoride solution in air but also two crystallization cycles under aerobic conditions.

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Experimental Part

1. *General.* All reactions were carried out under dry N_2 by using conventional *Schlenk* and septum techniques. All workups were performed in air. Solvents and chemicals were purchased from *Acros*, *Aldrich*, *Strem*, and *Merck*. Solvents were dried and distilled under N_2 according to standard techniques prior to use: THF over sodium/benzophenone; DMF and Et_3N over CaH_2; EtOH over Mg. All other chemicals were used as received. Racemic 1-[(dimethylamino)methyl]-2-(tributylstannyl)ferrocene (**1**) was prepared by a slightly modified known procedure [3c]. Melting points: *Büchi-530* melting point apparatus, not corrected. Flash column chromatography (FC): silica gel *F 60* from *Fluka* or *Merck*. TLC: *Merck-F-60* silica plates with a 364 nm fluorescence indicator. NMR Spectra: *Jeol FT-JNM-EX-270* (270 MHz) and *Bruker AMX-300* (300 MHz) spectrometers; in deuterated solvents and referenced to the residual proton signal of the particular solvent. Mass spectra: *Varian MAT-212* spectrometer. Elemental analyses: *Carlo-Erba* elemental analyzer, model *1108*.

2. rac-*1-[(1,3-Dihydro-1,3-dioxo-2*H-*isoindol-2-yl)methyl]-2-(tributylstannyl)ferrocene* (**2**). *Caution! All operations must be performed in a hood!* To a suspension of racemic **1** (17.48 g, 32.84 mmol) in DMF (35 ml) in a *Schlenk* tube capable to withstand a minimum pressure of 10 bar, MeI (2.30 ml, 5.34 g, 36.95 mmol) was added dropwise at r.t. The suspension was stirred for 30 min at r.t. until it became a clear orange soln. and heat evolution ceased. Excess MeI was then quenched with Et_3N (2.00 ml, 14.35 mmol). Solid potassium phthalimide (8.19 g, 44.21 mmol) was added, and the suspension was diluted with DMF (10 ml). The inhomogeneous mixture was stirred for 15 h at 100° in the closed *Schlenk* tube to become a nearly clear deep orange soln. after reaching the reaction temp. The endpoint of the reaction was indicated by the separation of two liquid phases. *Caution! Before opening, the* Schlenk *tube must slowly cool down to room temperature!* After such a cooling down to r.t., excess potassium phthalimide precipitated. The mixture was diluted with Et_2O, and excess potassium phthalimide was filtered off over a *D4*-sinter with vacuum suction. The filter cake was washed with Et_2O. The combined filtrate and washing soln. was diluted with AcOEt and the soln. washed eight times with brine until free of DMF, dried ($MgSO_4$), and concentrated to give nearly pure **2** (19.08 g, 92%), which was purified by FC (substance applied in eluent, hexanes/AcOEt 2:1): 17.45 g of pure racemic **2**. Red oil solidifying to a waxy semicrystalline mass upon standing. M.p. 65–67° (rac.). ^{1}H-NMR ($CDCl_3$, 270 MHz): 7.79 (*m*, H–C(4) and H–C(7) of $C_6H_4(CO)_2N$); 7.66 (*m*, H–C(5) and H–C(6) of $C_6H_4(CO)_2N$); 4.65 (*d*, ^2J = 14.53, 1 H, CH_2); 4.53 (*m*, 1 H, Cp); 4.43 (*d*, ^2J = 14.53, 1 H, CH_2); 4.26 ('*t*', 1 H, Cp); 4.11 (*s*, 5 H, Cp′); 3.91 (*m*, 1 H, Cp); 1.60–1.52 (not resolved *t*, 3 *Me*$CH_2CH_2CH_2$); 1.42–1.28 (not resolved *tt*, 3 $MeCH_2CH_2CH_2$); 1.20–1.09 (not resolved *qt*, 3 $MeCH_2CH_2CH_2$); 0.89 (*t*, ^3J = 7.27, 3 $MeCH_2CH_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$, 68 MHz): 167.78 ($C_6H_4(CO)_2N$); 133.74 (C(5) and C(6) of $C_6H_4(CO)_2N$); 132.08 (C(3a) and C(7a) of $C_6H_4(CO)_2N$); 123.08 (C(4) and C(7) of $C_6H_4(CO)_2N$); 88.51 (*d*, ^2J(C,Sn) = –38.2, C(1) of Cp); 75.13 (*d*, *J*(C,Sn) = –22.5, Cp); 71.98 (*d*, *J*(C,Sn) = –28.2, Cp); 71.16 (*d*, *J*(C,Sn) = –34.2, Cp); 70.48 (*d*, ^1J(C,Sn) = –29.9, C(2) of Cp); 68.66 (Cp′); 38.51 (CH_2); 29.31 (Me$CH_2CH_2CH_2$); 27.48 (*d*, ^2J(C,Sn) = –61.7, $MeCH_2CH_2CH_2$); 13.68 (*Me*$CH_2CH_2CH_2$); 10.95 (*d*, ^1J(C,Sn) = –320.8, $MeCH_2CH_2CH_2$). FD-MS (pos.; $CHCl_3$): 634 (100, M^+ with respect to ^{56}Fe). Anal.calc. for $C_{31}H_{41}FeNO_2Sn$ (634.23): C 58.71, H 6.52, N 2.21; found: C 58.47, H 6.75, N 2.20.

3. rac-*1-[(1,3-Dihydro-1,3-dioxo-2*H*-isoindol-2-yl)methyl]-2-phenylferrocene* (**5**). *Caution! All operations must be performed in a hood! All glassware for this reaction must be cleaned in a base bath before use and rinsed with dist. H_2O only (not with acid or acetone!!), and heated in an oven at 200° overnight!* The reaction tolerates traces of moisture, but air must be vigorously excluded. Into a *Schlenk* tube were weighed under air first **2** (8.209 g, 12.943 mmol), then $[Pd_2(dba)_3]\cdot CHCl_3$ (335 mg, 0.324 mmol), then CuI (1.235 g, 6.485 mmol), and finally $AsPh_3$ (595 mg, 1.943 mmol), in this order. After three evacuation–N_2 flushcycles, the mixture was suspended in DMF (55 ml), and then freshly distilled iodobenzene (2.80 ml, 5.096 g, 24.979 mmol) was added. The mixture was stirred for 14 h at 70° until precipitation of 'palladium black' indicated the endpoint of the reaction. Alternatively, the reaction was monitored by TLC (hexanes/AcOEt 2:1; R_f(**2**) 0.56 and R_f(**5**) 0.42). After cooling to r.t., KF (*ca.* 2.2 g) and then dist. H_2O (*ca.* 20 ml) were added into the open flask, whereupon the mixture became warm and was stirred for 30 min at r.t. to ensure total cleavage of all organostannane compounds. All solid residues of the black suspension were filtered off over a *D3* sinter with cellulose flakes by vacuum suction. The filter cake was washed with AcOEt. The combined filtrate and washing soln. was diluted with AcOEt and the soln. washed eight times with brine until free of DMF, dried ($MgSO_4$), and concentrated to give an orange microcrystalline squash (*ca.* 10.91 g) containing nearly exclusively iodobenzene and **5**. The crude product was dissolved in a minimum amount of hot AcOEt, the soln. was layered with pentane, and crystallization was completed overnight at −30°. After a second recrystallization of the same kind finally nearly pure racemic **5** (4.012 g, 74%) was obtained as deep orange crystals. *After recrystallization, the product was not free of catalyst or ligand traces, so it must also be considered as potentially toxic!* The combined mother liquors were crystallized at −30° from AcOEt only to give a crystal mixture mostly consisting of racemic **5**. From this mixture, one single crystal of racemic **5**, one of intermediate *trans*-$[Pd^{II}(I)(Ph)(AsPh_3)_2]$ (**7**), one of *trans*-$[Pd^{II}(I)_2(AsPh_3)_2]$ (**8**) and one of rac-*2,2′-bis[(1,3-dihydro-1,3-dioxo-2*H*-isoindol-2-yl)methyl)]-1,1′-biferrocene* (**9**) were isolated under a microscope by crystal color and shape, which were all suitable for X-ray crystal-structure determination (see below). Crystal sizes [mm]: 0.35 × 0.13 × 0.11 (**5**), 0.11 × 0.10 × 0.07 (**7**), 0.18 × 0.18 × 0.09 (**8**), and 0.28 × 0.14 × 0.08 (**9**). **5**: M.p. 146° (rac.). ^{1}H-NMR ($CDCl_3$, 270 MHz): 7.84–7.79 (*m*, H–C(4) and H–C(7) of $C_6H_4(CO)_2N$); 7.66 (2*m*, H–C(5) and H–C(6) of $C_6H_4(CO)_2N$, and 2 H_o of Ph); 7.43–7.26 (*m*, 2 H_m and 1 H_p of Ph); 4.90 (*d*, ^2J = 14.8, 1 H, CH_2); 4.70 (*d*, ^2J = 14.8, 1 H, CH_2); 4.39 ('*d*', 2 H, Cp); 4.20 ('*t*', 1 H, Cp); 4.12 (*s*, 5 H, Cp′). ^{13}C{^{1}H}-NMR ($CDCl_3$, 68 MHz): 167.95 ($C_6H_4(CO)_2N$); 137.58 (C_{ipso} of Ph); 133.89 (C(5) and C(6) of $C_6H_4(CO)_2N$); 131.95 (C(3a) and C(7a) of $C_6H_4(CO)_2N$); 129.63 (C_m of Ph); 127.96 (C_o of Ph); 126.52 (C_p of Ph); 123.22 (C(4) and C(7) of $C_6H_4(CO)_2N$); 87.96 (C(2) of Cp); 82.35 (C(1) of Cp); 70.17 (Cp′); 69.17 (Cp); 68.83 (Cp); 67.26 (Cp); 36.09 (CH_2). FD-MS (pos.; $CHCl_3$): 422 (100, M^+ with respect to ^{56}Fe). A correct elementary analysis could not be obtained.

4. rac-*1-(Aminomethyl)-2-phenylferrocene* (**11**). A suspension of **5** (5.814 g, 13.80 mmol) and of hydrazine hydrate (7.00 ml, 7.210 g, 144.03 mmol) in EtOH *p.a.* (100 ml) was refluxed for 75 min at 95°. White phthalazine-1,4-dione started to precipitate once the reaction temp. was reached. After cooling to r.t., Et_2O was added, the solid phthalazine-1,4-dione sucked off and washed with Et_2O, and the red soln. combined with the washing soln. concentrated. The residue was redissolved in Et_2O and the org. phase washed once with brine (made alkaline with NaOH), dried ($MgSO_4$), and concentrated to give crude product (4.031 g, quant.) which was purified by FC (hexanes/CH_2Cl_2 1:5 + 10% Et_3N): 3.584 g (89%) of pure racemic **11**. Red oil. ^{1}H-NMR ($CDCl_3$, 270 MHz): 7.57–7.50 (*m*, 2 H_o of Ph); 7.36–7.19 (2*m*, 2 H_m and H_p of Ph); 4.44 ('*t*', 1 H, Cp); 4.33 ('*t*', 1 H, Cp); 4.21 ('*t*', 1 H, Cp); 4.09 (*s*, 5 H, Cp′); 3.82 (*d*, ^2J = 14.1, 1 H, CH_2); 3.76 (*d*, ^2J = 14.1, 1 H, CH_2); 1.60 (br. *s*, NH_2). ^{13}C{^{1}H}-NMR ($CDCl_3$, 68 MHz): 138.30 (C_{ipso} of Ph); 128.64 (C_m of Ph); 127.90 (C_o of Ph); 126.04 (C_p of Ph); 88.13 (C(1) of Cp); 86.41 (C(2) of Cp); 69.64 (Cp′ and Cp); 68.18 (Cp); 66.56 (Cp); 40.22 (CH_2). FD-MS (pos.; $CHCl_3$): 292 (100, $[M + H]^+$ with respect to ^{56}Fe). Anal. calc. for $C_{17}H_{17}FeN$ (291.17): C 70.13, H 5.88, N 4.81; found: C 70.12, H 5.92, N 4.79.

5. rac-*1-(Aminomethyl)-2-(cyclohexa-2,5-dienyl)ferrocene* (**12**). To freshly condensed liquid ammonia (130 ml) was canuled a precooled soln. of racemic **11** (2.254 g, 7.74 mmol) in EtOH (10 ml) and THF (45 ml) at −78°. Then Li (670 mg, 96.53 mmol) was added, and the soln. was stirred vigorously at −78°. The blue color of solvated electrons persisted for 1 h before the reaction was quenched with NH_4Cl (5.703 g, 106.62 mmol). After evaporation of ammonia, the residue was poured into brine (made alkaline

with NaOH), the aq. phase extracted twice with Et_2O, and the combined org. phase dried overnight (Na_2SO_4) and concentrated: 2.184 g (96%) of racemic **12** (free of any starting material by NMR). Red oil which was not further purified. ^{1}H-NMR ($CDCl_3$, 270 MHz): 6.00–5.76 (2*m*, H–C(2) and H–C(6) of C_6H_7); 5.76–4.48 (2*m*, H–C(3) and H–C(5) of C_6H_7); 4.15 (*m*, 1 H, Cp); 4.10 (*s*, 5 H, Cp′); 4.04 (*m*, H–C(1) of C_6H_7); 4.00 (‘*t*’, 1 H, Cp); 3.96 (*m*, 1 H, Cp); 3.63 (*d*, $^2J = 14.2$, 1 H, CH_2); 3.54 (*d*, $^2J = 14.2$, 1 H, CH_2); 2.68–2.65 (*m*, CH_2(4) of C_6H_7). ^{13}C{^{1}H}-NMR ($CDCl_3$, 68 MHz): 128.85 (C(3) or C(5) of C_6H_7); 128.1 (C(5) or C(3) of C_6H_7); 124.41 (C(2) or C(6) of C_6H_7); 123.17 (C(6) or C(2) of C_6H_7); 91.07 (C(2) of Cp); 87.91 (C(1) of Cp); 68.65 (Cp′); 67.65 (Cp); 67.44 (Cp); 65.58 (Cp); 39.84 (CH_2); 33.90 (C(1) of C_6H_7); 25.92 (C(4) of C_6H_7). FD-MS (pos.; $CHCl_3$): 294 (100, $[M+H]^+$ with respect to ^{56}Fe).

6. *Crystal Structure Determinations*[4]). Crystal parameters, data collection, and structure refinement details are summarized in *Table 5*. Intensity data were collected at 100 K on a *Bruker-Nonius-KappaCCD* diffractometer (MoK_α radiation, λ 0.71073 Å, graphite monochromator). All structures were solved by direct methods [9] and refined by full-matrix least-squares procedures on F^2. All non-H-atoms were refined with anisotropic displacement parameters. Absorption corrections were performed on the basis of multiple scans with SADABS [9c]. All H-atoms were placed in positions of optimized geometry; their isotropic displacement parameters were tied to the equivalent isotropic displacement parameters of their

Table 5. *Crystallographic Data for* **5**, **7**, **8** *and* **9**·*0.65 AcOEt*. All measured at 100 K.

	5	**7**	**8**	**9**·0.65 AcOEt
Empirical formula	$C_{25}H_{19}FeNO_2$	$C_{42}H_{35}As_2IPd$	$C_{36}H_{30}As_2I_2Pd$	$C_{40.6}H_{33.2}Fe_2N_2O_{5.3}$
M_r	421.26	922.84	972.64	745.59
Crystal system	orthorhombic	orthorhombic	triclinic	monoclinic
Space group	*Pbca* (no. 61)	*Pbca* (no. 61)	$P\bar{1}$ (no. 2)	$P2_1/_C$ (no. 14)
a [Å]	16.318(2)	19.503(2)	10.1917(7)	13.310(2)
b [Å]	7.9306(6)	10.846(2)	12.6708(9)	7.3722(6)
c [Å]	29.038(3)	33.315(3)	13.1838(9)	34.450(3)
α [°]	90	90	84.614(8)	90
β [°]	90	90	77.726(7)	97.95(1)
γ [°]	90	90	78.764(6)	90
V [Å^3]	3757.9(7)	7047(2)	1629.3(2)	3347.9(6)
Z	8	8	2	4
ρ [g/cm^3] (calc.)	1.489	1.740	1.983	1.479
μ [mm^{-1}]	0.825	3.296	4.504	0.917
F (000)	1744	3616	928	1541
T_{min}; T_{max}	0.763; 0.910	0.654; 0.790	0.469; 0.667	0.750; 0.929
2θ interval [°]	$7.1 \le 2\theta \le 555.8$	$7.3 \le 2\theta \le 54.2$	$6.5 \le 2\theta \le 55.8$	$7.0 \le 2\theta \le 51.4$
Lim. indices	$-21 \le h \le 21$; $-10 \le k \le 10$; $-38 \le l \le 38$	$-24 \le h \le 25$; $-13 \le k \le 13$; $-41 \le l \le 42$	$-13 \le h \le 13$; $-16 \le k \le 16$; $-17 \le l \le 17$	$-16 \le h \le 16$; $-8 \le k \le 8$; $-42 \le l \le 42$
Coll. refl.	37177	51608	35711	38439
Indep. refl.	4474	7744	7759	6250
Obs. refl. ($I_0 \ge 2\sigma(I)$)	3677	6022	6408	4956
No. ref. param.	262	415	373	494
wR_2 (all data)	0.0700	0.0893	0.0488	0.1076
R_1 ($I_0 \ge 2\sigma(I)$)	0.0304	0.0449	0.0219	0.0459
GooF (on F^2)	1.030	1.115	1.026	1.022
Max.; min. res. electr. density	0.330; −0.275	1.863; −0.910	0.837; −0.930	0.857; −0.933

[4]) CCDC-618850 (for **5**), CCDC-618851 (for **7**), CCDC-618852 (for **8**), and CCDC-618853 (for **9**·0.65 AcOEt) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

corresponding carrier atoms by a factor of 1.2 or 1.5, resp. Compound **9** crystallized with *ca.* 0.65 molecules of AcOEt per formula unit, which are disordered; two preferred positions could be refined, which are occupied by 44.5(6)% and 20.5(6)% in the crystal. The unit cell of the Pd-complex **8** contains two symmetry-independent molecule halves in the asymmetric unit, which are each located on crystallographic inversion centers. For Pd^{II} intermediate **7**, the highest maximum of residual electron density is located in *trans* position to the iodo ligand. Distance and location of this maximum suggest that the crystal structure contains traces of the corresponding diiodo complex **8** of not more than 3%. Attempts to consider these traces by a disorder model did not lead to satisfying results.

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