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Phosphinoferrocenyl-terminated amidoamines: Synthesis and catalytic utilization in palladium-mediated C–C bond forming reactions

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Abstract

1′-(Diphenylphosphino)-1-(*N*-butylcarbamoyl)ferrocene (**P1**) and the analogous higher amides **P2–4** related to the first-generation PAMAM dendrimers bearing up to four 1′-(diphenylphosphino)ferrocen-1-yl terminal groups were synthesized by amidation of the respective (poly)amines with 1′-(diphenylphosphino)ferrocenecarboxylic acid (Hdpf). Testing of amides **P1–4** as ligands for palladium-catalyzed Suzuki and Heck coupling reactions has shown that these amidophosphines preserve the activity of the single phosphinoferrocenyl unit, giving rise to active catalysts in both C–C forming reactions. Even for such relatively small systems, a positive influence of the dendritic assembly was notable as the compounds bearing a higher number of the phosphinoferrocenyl termini afforded faster reacting catalytic systems at the same palladium loading and P-to-Pd ratio.

Keywords: Amides; Phosphines; PAMAM; Dendrimers; Heck coupling; Suzuki coupling; Palladium

1. Introduction

The use of dendritic and star-shaped molecules as supporting scaffolds to catalytic systems has attracted recent attention mainly because the resulting multifunctional catalysts often react as their homogeneous, low-molecular counterparts but can be recovered from the reaction mixture by, for example, nanofiltration and subsequently recycled [1]. One of the possible approaches toward such catalysts relies on introducing the active moieties onto the periphery of the supporting framework. This method allows incorporation of a high number of functional termini and provides catalysts that offer a good access for the substrate to the active sites from the reaction medium. Quite often, however, the end-groups form specific microenvironments at the functionalized surface and thus impart unusual reactivity [1,2].

In view of our previous work aimed at the preparation, coordination behavior and catalytic chemistry of ferrocene-based phosphinocarboxylic acids [3], we decided to explore their use in the preparation of dendrimer-like assemblies featuring *several* covalently bonded terminal ferrocene moieties. In their synthesis, we made use of 1′-(diphenylphosphino)ferrocenecarboxylic acid (Hdpf) [4] and its smooth reaction with terminal NH_2 groups of first-generation poly(amido-amines) (PAMAM) [5,6]. Our interest has been stimulated largely by a possible utilization of such compounds in catalysis since Hdpf [7] and its simple amides [8,9] have already proved active catalyst components for the palladium-catalyzed Suzuki cross-coupling reaction.

It should be noted that our approach complements the one coined by Togni et al., who used the amidation reaction of carboxy-terminated dendrimers with chiral ferrocene diphosphines equipped with amine anchoring groups [10]. The modification of amine end-groups in dendrimers with ferrocenecarboxylic acids aimed at the preparation of redox-active dendritic molecules is also well documented [11].

In this work, we report the synthesis and characterization of a family of four (poly)amides bearing one to four

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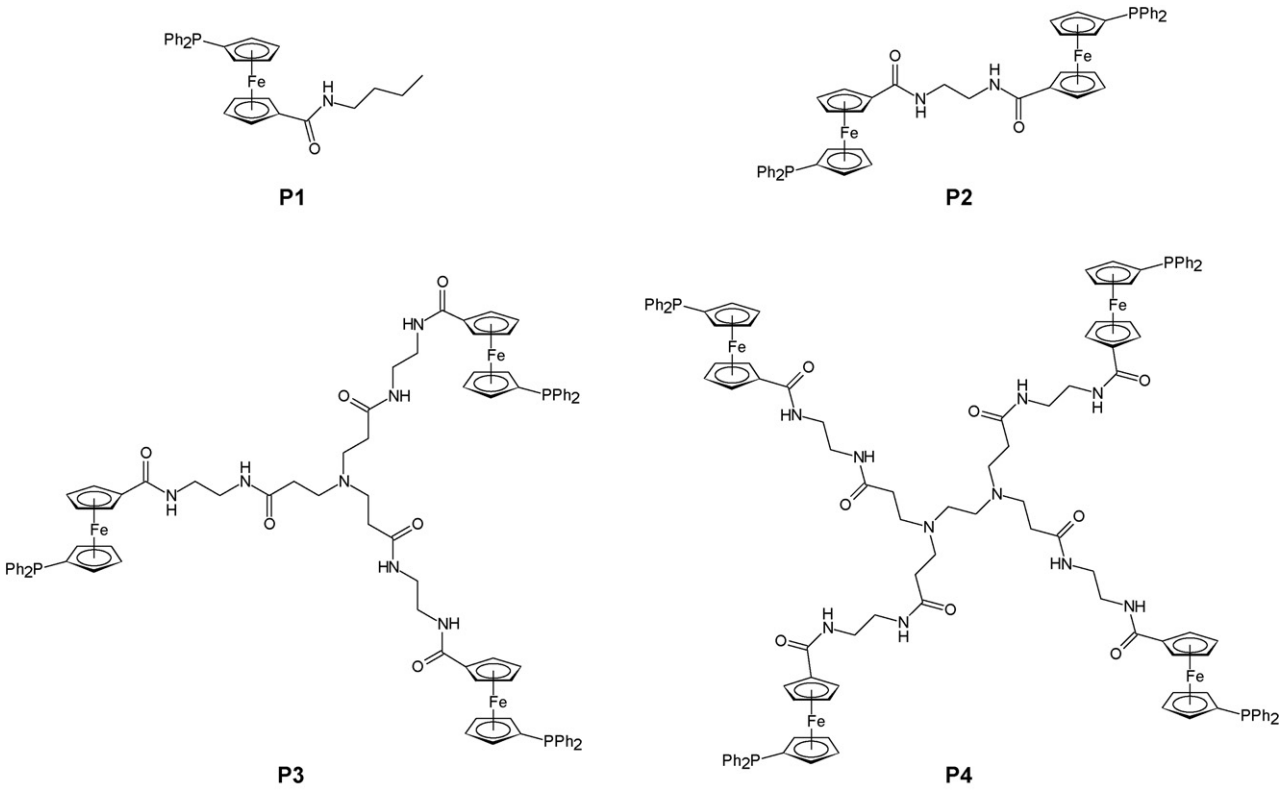


Scheme 1. (Poly)amides with terminal phosphinoferrocenyl groups.

1′-(diphenylphosphino)ferrocen-1-yl groups (compounds **P1**–**P4** in Scheme 1) and the results of testing these compounds as ligands to palladium-mediated C–C coupling reactions, viz. Heck and Suzuki cross-coupling.

2. Results and discussion

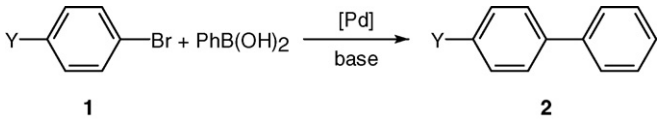
2.1. Preparation of the phosphinoamide dendrimers

Compounds **P1**, **P3** and **P4** have been synthesized by amidation of the appropriate amines with 1′-(diphenylphosphino)ferrocenecarboxylic acid (Hdpf) [4] in the presence of peptide coupling agents [12] as previously described for the diamide **P2** [9]. The newly prepared compounds have been characterized by the conventional spectral methods and their composition corroborated by mass spectra that show signals due to molecular ions (M^+ or $[M+H]^+$ depending on the ionization method; see Section 4). The NMR spectra of the amides also confirm the formulation by combining characteristic signals attributable to the chemically equivalent 1′-(diphenylphosphino)ferrocen-1-yl moieties with those of the PAMAM backbone. Besides, the presence of the amide linking groups is clearly manifested by the characteristic strong amide I and amide II bands in the IR spectra at around 1630 and 1540 cm^{-1}, respectively. Once characterized, compounds **P1**–**4** have been tested as the ligands for Suzuki cross-coupling [13,14] and the Heck reaction [15,16] with model substrates.

2.2. The Suzuki cross-coupling

For initial testing in the Suzuki reaction, we chose phosphines **P1** and **P4** as the ligands, and the coupling of 4-bromotoluene (**1a**) with an excess of phenylboronic acid (1.5 molar equiv.) to give 4-methylbiphenyl (**2a**, Scheme 2). The reactions were performed in dioxane at 100 °C for 16 h with varying Pd loading but at the *constant* Pd:P ratio of 1:1.2. As indicated by the results summarized in Table 1, the coupling reaction proceeded almost quantitatively even with 0.1 mol% of the palladium catalysts. Lowering of the catalyst loading by one order of magnitude significantly reduced the conversion and, particularly, the reproducibility of the catalytic results. This can be attributed to a poorly reproducible formation of the active species from the tiny amounts of the catalyst components added to the reaction mixture. At 0.001 mol% palladium loading, the coupling reaction occurred in only a negligible extent.

The conversions attained in the absence of a supporting ligand were only about 5% after 1–2 h and did not increase any further upon prolonged reacting times (Fig. 1). It follows that the amidophosphine ligands play a vital role in catalytic acti-



Scheme 2. Suzuki reaction of aryl bromides [Y = Me (a), OMe (b), C(O)Me (c), and NO_2 (d)].

Table 1
Effect of palladium loading on the Suzuki coupling of **1a** with phenylboronic acid to give **2a**[a]

Ligand	Conversion (%)	
w(Pd) (mol%)	**P1**	**P4**
0.5	100	100
0.1	96	97
0.01[b]	ca. 40	45-75[c,d]
0.001[b]	ca. 6	ca. 5

[a] All experiments have been performed at a Pd:P ratio of 1:1.2 and in the presence of 1.5 molar equivalents of phenylboronic acid (100 °C/16 h in dioxane). The results are an average of two independent runs unless noted otherwise.
[b] The conversions at low Pd-loadings were poorly reproducible.
[c] The range for five independent runs.
[d] Reactions with 0.01 mol% of $Pd(OAc)_2$ at Pd:P ratios = 2.4 and 4.8 gave **2a** with 12% and 17% conversions, respectively.

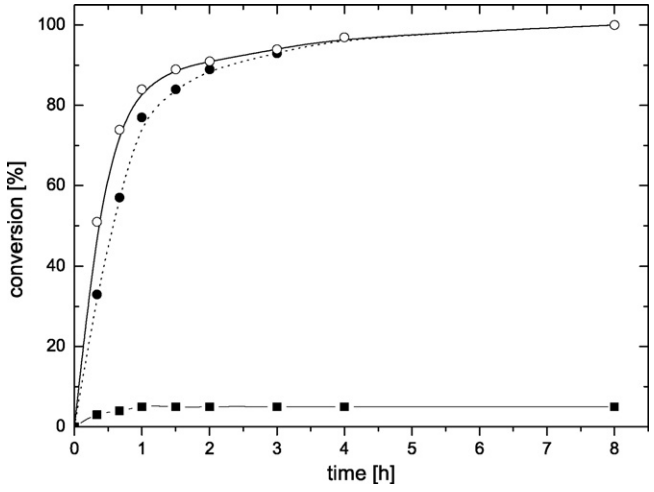


Fig. 1. Kinetic profiles of the Suzuki cross-coupling reactions of 4-bromotoluene with phenylboronic acid. The reactions were performed at a 0.1 mol% palladium loading with **P1** (●) and **P4** (◯) as the ligands in amounts corresponding to a Pd:P molar ratio of 1:1.2. For a comparison, the kinetic profile for a similar reaction catalyzed only by 0.1 mol% of $Pd(OAc)_2$ (i.e., without any supporting ligand) is also included (■). The experimental points are an average of two independent runs. For detailed conditions, see Section 4.

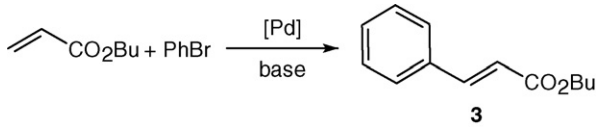
vation of the metal source and, perhaps, also in stabilization of the formed active species, particularly in the non-coordinating solvent used.

In order to establish a possible dendritic effect, we have subsequently compared the reaction rates for the catalysts based on **P1** and **P4**. Kinetic profiles of the coupling reactions performed at catalyst loading of 0.1 mol% and at a Pd:P ratio of 1:1.2 are shown in Fig. 1. Although both catalytic systems gave the coupling product quantitatively within 8 h, the initial reaction rates were different. The **P4**-based catalyst reacted faster than that generated from the simple phosphinoamide **P1**. In order to quantify the observed differences, the kinetic profiles were fitted by sigmoidal curves. Analysis of the "linear" branch at low conversions led to the initial reaction rates 1.00(2) mmol h^{-1} for **P1**, and 1.50(6) mmol h^{-1} for **P4** at the *same* phosphorus and palladium "loadings".

Finally, the scope of the reaction has been probed with a series of activated (**1c**,**d**) and deactivated (**1a**,**b**) aryl bromides (Table 2). In the presence of 0.1 mol% palladium-phosphine catalyst, the reactions with **1a–d** and all phosphines **P1–4** proceeded with complete or near-to-complete conversions. However, the higher-generation phosphines **P2–4** performed slightly better than **P1**, particularly for the deactivated substrates. Similar reactions with the corresponding aryl chlorides (4-ClC_6H_4Y) did not proceed at all (Y = Me, OMe, and C(O)Me) or gave the coupling product in trace amounts (Y = NO_2). Even after increasing the amount of the palladium catalyst to 1 mol%, 4-chloronitrobenzene afforded 4-nitrobiphenyl (**2d**) with only 22% conversion.

2.3. The Heck reaction

For testing in the Heck reaction we chose the coupling of *n*-butyl acrylate with bromobenzene to give *n*-butyl cinnamate (**3**) as the model reaction (Scheme 3). Since the reactions were carried out at 155 °C, the halide as the most volatile component was used in excess. Unless noted otherwise, the reactions were performed with catalysts generated *in situ* from 0.5 mol% of palladium(II) acetate and the ligand in amounts corresponding to Pd:P ratio of 1:1.2. Similarly to the previous case, we started with **P1** as the simplest donor, trying to optimize the reaction con-



Scheme 3. Heck reaction of butyl acrylate with bromobenzene to give butyl cinnamate.

Table 2
Survey of aryl bromides in the Suzuki cross-coupling of aryl bromides with $PhB(OH)_2$[a]

Ligand	Conversion to biphenyls **2a–d** (%)			
Substrate	**P1**	**P2**	**P3**	**P4**
4-BrC_6H_4Me (**1a**)	96	Quant.	90	97
4-BrC_6H_4OMe (**1b**)	91	92	Quant.	Quant.
4-$BrC_6H_4C(O)Me$ (**1c**)	92	Quant.	Quant.	Quant.
4-$BrC_6H_4NO_2$ (**1d**)	Quant.	Quant.	Quant.	Quant.

[a] Catalytic experiments were performed in the presence of 0.1 mol% of palladium(II) acetate and at a Pd:P of ratio 1:1.2 (100 °C/16 h in dioxane). The results are an average of two independent runs.

Table 3
Survey of the reaction solvents and bases for the Heck reaction of butyl acrylate with bromobenzene[a]

Base	Solvent	Conversion (%)
NaOAc	DMF	24
Na_2CO_3	DMF	26
K_2CO_3	DMF	19
Cs_2CO_3	DMF	7
None	DMF	0
NaOAc[b]	DMF	22
NaOAc[b]	DMA	10

[a] Reaction with 0.5 mol%. Pd and **P1** at 155 °C for 24 h. DMF = *N,N*-dimethylformamide, DMA = *N,N*-dimethylacetamide. For detailed conditions, see Section 4.
[b] Catalyst loading lowered to 0.1 mol% of Pd.

ditions via changing the base additive and the reaction solvent (Table 3 and Fig. 2).

An inspection of several bases typically used in Heck reactions showed similar activity for sodium and potassium carbonates and sodium acetate, while the use of Cs_2CO_3 led to significantly lower conversions. The reaction performed in the absence of an external base did not give any coupling product. According to a GC–MS analysis of the reaction mixture, the observed decline in the amount of the formed butyl cinnamate at prolonged reaction times can be explained by decomposition under the reaction conditions (e.g., polymerization) rather than formation of the doubly arylated product. Furthermore, the results collected in Table 3 indicate that reactions performed in DMF solvent proceed with higher yields that those in DMA. Similarly to the Suzuki reaction (see above), the Heck coupling practically stopped when no supporting amidophosphine ligand was added to the reaction mixture. For instance, the conversion of the reaction performed under identical conditions but with only 0.5 mol% palladium(II) acetate as the catalyst was ca. 2% after 8 h.

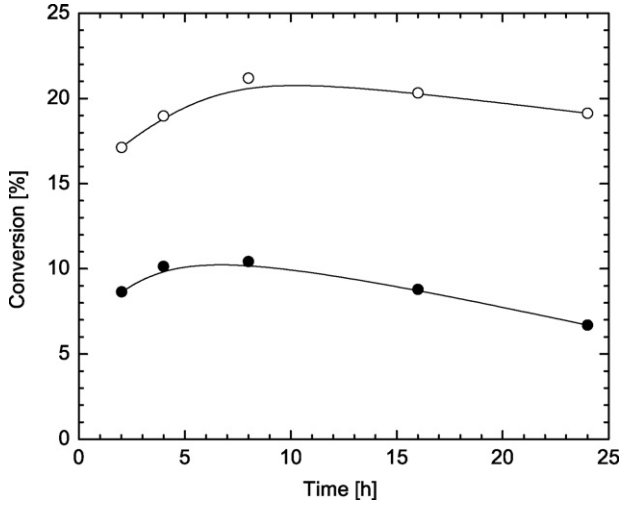


Fig. 2. Comparison of kinetic profiles for the Heck coupling performed with **P1** as the ligand and K_2CO_3 (◯) or Cs_2CO_3 (●) as the base (solvent DMF).

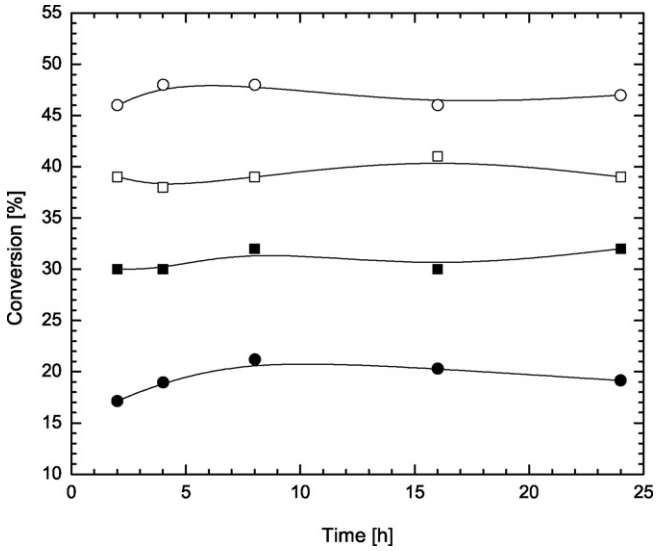


Fig. 3. Kinetic profiles for the Heck coupling between *n*-butyl acrylate and bromobenzene catalyzed with 0.5 mol% palladium catalyst prepared from $Pd(OAc)_2$ and phosphines **P1** (●), **P2** (■), **P3** (□), and **P4** (◯). The lines are shown as a "guide for an eye" and do not represent any fit. For detailed reaction conditions, see Section 4.

The results obtained by examination of **P1–4** as the phosphine components proved more interesting. All reactions performed at a Pd:P molar ratio of 1:1.2 showed similar kinetic profiles (Fig. 3): The reactions were completed relatively fast (within ca. 5–8 h), then approaching a state with practically constant composition of the reaction mixture. However, the conversions reached with the individual ligands were significantly different, increasing with the number of the phosphinoferrocenyl termini (cf. the conversions 21% (**P1**), 32% (**P2**), 39% (**P3**), and 48% (**P4**) after 8 h).

These results indicate that the donors with a higher number of terminal phosphino groups produce catalytic species in either relatively higher amounts or, more likely, with a higher activity. Another plausible explanation is the formation of dendrimer-supported palladium nanoparticles, which have been shown to be highly active in C–C bond forming cross-coupling reactions [1i,1j, 14a, 14d, 14e, 16a, 16b, 17]. This assumption is in line with the observed reactivity since a larger dendritic assembly can provide a better stabilization to a metallic particle.

3. Conclusions

In summary, we have demonstrated that simple polyamidoamines (first-generation PAMAM dendrimers) are suitable scaffolds for the preparation of monodisperse polyfunctional molecules bearing phosphinoferrocenyl termini via their amidation reaction with 1′-(diphenylphosphino)ferrocenecarboxylic acid (Hdpf). Catalytic testing of the resulting compounds containing up to four ferrocene units (**P1–4**) has shown that single ligand units preserve their activity. However, even among such relatively small systems, we have observed positive cooperativity of the functional termini as the compounds bearing a higher number of the phosphinoferrocenyl groups gave rise to faster reacting and more robust catalytic systems.

4. Experimental

4.1. General comments

All syntheses were performed under an argon or nitrogen atmosphere and with exclusion of the direct daylight. Hdpf [4], the amidoamines [18] and compound **P2** [9] have been synthesized by the literature procedure. Dichloromethane was dried over calcium hydride and distilled. Dioxane was distilled from sodium under argon atmosphere. Dry DMF and DMA over molecular sieves were purchased from Fluka and used without further purification. Sodium acetate was freshly melted in order to remove traces of water. Other chemicals and solvents were used as received from commercial sources (Fluka, Aldrich; solvents from Penta).

NMR spectra were measured on a Varian UNITY Inova 400 spectrometer at 25 °C. Chemical shifts (δ/ppm) are given relative to internal tetramethylsilane (^{1}H and ^{13}C) or to an external 85% aqueous H_3PO_4 (^{31}P). In addition to the standard notation of the signal multiplicity, vt and vq are used to distinguish virtual multiplets arising in magnetically non-equivalent AA′BB′ and AA′BB′X spin systems of the amide- and phosphorus-substituted cyclopentadienyl rings (*Note*: fc = ferrocen-1,1′-diyl). IR spectra were recorded on an FT IR Nicolet Magna 760 instrument in the range of 400–4000 cm^{-1}. Mass spectra were obtained on a ZAB-EQ (VG Analytical) spectrometer. Electrospray (ESI) mass spectra were recorded with an Esquire 3000 (Bruker) spectrometer (methanol solutions) or a Q-TOF micro (Waters) spectrometer (in MeOH–water 9:1). Melting points were determined on a Kofler hot stage. The instrumentation used in catalytic tests is described below.

4.2. Preparation of 1′-(N-butylcarbamoyl)-1-(diphenylphosphino)ferrocene (**P1**)

N-(3-Dimethylaminopropyl)-*N*′-ethylcarbodiimide (47 mg, 0.30 mmol) was added to an ice-cooled solution of Hpdf (104 g, 0.25 mmol) and 1-hydroxybenzotriazole (41 mg, 0.30 mmol) in dry dichloromethane (5 mL). Stirring was continued for 30 min at 0 °C. After adding of *n*-butylamine (0.03 mL, 0.30 mmol), the cooling bath was removed, and the mixture was stirred at room temperature overnight. The reaction mixture was extracted with 1% aqueous citric acid, saturated aqueous $NaHCO_3$, and brine. The organic phase was dried over $MgSO_4$ and evaporated. The residue was purified by column chromatography on silica gel eluting first with dichloromethane and then with dichloromethane/methanol (50:1). The fraction from dichloromethane/methanol was collected and evaporated to give **P1** as an orange solid. Yield: 105 mg (90%).

M.p. 58–60 °C (ethyl acetate/hexane). ^{1}H NMR ($CDCl_3$): 0.92 (t, $^3J_{HH}$ = 7.3 Hz, 3 H, CH_3), 1.38 (m, 2 H, CH_2), 1.53 (m, 2 H, CH_2), 3.31 (dt, $^3J_{HH}$ = 5.9 (CH_2), $^3J_{HH}$ = 7.1 (NH) Hz, 2 H, CH_2), 4.06 (vq, J = 1.9 Hz, 2 H, fc), 4.19 (vt, J = 1.9 Hz, 2 H, fc), 4.42 (vt, J = 1.8 Hz, 2 H, fc), 4.58 (vt, J = 2.0 Hz, 2 H, fc), 5.95 (m, 1 H, NH), 7.30–7.40 (m, 10 H, PPh_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 13.80 (CH_3), 20.16, 31.97, 39.32 (3 × CH_2); 69.43, 71.35 (2 × CH of fc); 72.78 (d, J_{PC} = 4 Hz), 74.27 (d, J_{PC} = 15 Hz) (2 × CH of fc); 76.88 (d, $^1J_{PC}$ = 6 Hz, C_{ipso} of fc), 77.16 (C_{ipso} of fc), 128.26 (d, J_{PC} = 6 Hz), 128.74, 133.41 (d, J_{PC} = 20 Hz) (3 × CH of PPh_2); 138.31 (d, $^1J_{PC}$ = 9 Hz, C_{ipso} of PPh_2), 169.63 (C=O). ^{31}P{^{1}H} NMR ($CDCl_3$): −16.9. IR (Nujol): $\tilde{\nu}$/cm^{-1} 3334 (m) (ν_{NH}), 1625 (vs) (amide I), 1544 (vs) (amide II), 1298 (s), 1225 (w), 1192 (w), 1159 (m), 1026 (m), 830 (s), 740 (s), 699 (s), 637 (w), 501 (s), 452 (m). EI + MS: *m*/*z* 469 (100, M^+), 412 (47, $[M–Bu]^+$), 400 (24), 321 (78), 268 (40), 201(82), 171 (31), 121 (14). HR MS (EI+) calcd. for $C_{27}H_{28}{}^{56}FeNOP$ (M^+): 469.1258, found 469.1252. FAB+ MS (3-nitrobenzyl alcohol matrix): *m*/*z* 486 ($[M + O + H]^+$), 469 (M^+), 370, 321, 305, 285.

4.3. Preparation of $N(CH_2CH_2C(O)NHCH_2CH_2NHC(O)fcPPh_2)_3$ (**P3**)

Amide **P2** was obtained by the same procedure as described for **P1**, starting with Hpdf (0.830 g, 2.00 mmol), 1-hydroxybenzotriazole (0.270 g, 2.00 mmol), *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide (0.310 g, 2.00 mmol), and $N(CH_2CH_2C(O)NHCH_2CH_2NH_2)_3$ (0.230 g, 0.65 mmol). Column chromatography was carried out on alumina using first dichloromethane, then dichloromethane/ethanol (50:1) and finally dichloromethane/ethanol (20:1). Evaporation under vacuum of the fraction from dichloromethane/ethanol (20:1) gave pure **P3** as an orange solid foam. Yield: 0.577 g (57%).

^{1}H NMR (DMSO): δ 2.20 (t, $^3J_{HH}$ = 6.5 Hz, 6 H, CH_2), 2.62 (bs, 6 H, CH_2), 3.20 (m, 12 H, CH_2), 4.04 (vq, J = 1.9 Hz, 6 H, fc), 4.11 (vt, J = 1.9 Hz, 6 H, fc), 4.36 (vt, J = 1.8 Hz, 6 H, fc), 4.70 (vt, J = 1.9 Hz, 6 H, fc), 7.26–7.38 (m, 30 H, PPh_2), 7.87 (t, $^3J_{HH}$ = 5.4 Hz, 3 H, NH), 7.98 (t, $^3J_{HH}$ = 5.1 Hz, 3 H, NH). ^{13}C{^{1}H} NMR (DMSO): δ 32.99, 38.45, 38.59, 48.95 (4 × CH_2); 68.88, 71.14 (2 × CH of fc); 72.82 (d, J_{PC} = 4 Hz), 73.45 (d, J_{PC} = 15 Hz) (2 × CH of fc); 76.57 (d, $^1J_{PC}$ = 9 Hz, C_{ipso} of fc), 77.20 (C_{ipso} of fc), 128.22 (d, J_{PC} = 7 Hz), 128.56, 132.92 (d, J_{PC} = 20 Hz) (3 × CH of PPh_2); 138.28 (d, $^1J_{PC}$ = 10 Hz, C_{ipso} of PPh_2), 168.44, 171.50 (2 × C=O). ^{31}P{^{1}H} NMR (DMSO): δ −18.2. IR (Nujol): $\tilde{\nu}$/cm^{-1} 3276 (m) (ν_{NH}), 1635 (vs) (amide I), 1539 (vs) (amide II), 1433 (s), 1300 (s), 1261 (vs), 1184 (m), 1160 (m), 1094 (vs), 1026 (vs), 869 (w), 802 (vs), 742 (s), 696 (vs), 636 (w), 619 (w), 588 (w), 570 (w), 496 (s), 452 (m). ESI ± MS: *m*/*z* 1548 ($[M + H]^+$), 1583 ($[M + Cl]^-$). HR MS (ESI+) calcd. for $C_{84}H_{85}{}^{56}Fe_3N_7O_6P_3$ ($[M + H]^+$): 1548.3822, found 1548.3866.

4.4. Preparation of $(CH_2N(CH_2CH_2C(O)NHCH_2CH_2NHC(O)fcPPh_2)_2)_2$ (**P4**)

N-(3-Dimethylaminopropyl)-*N*′-ethylcarbodiimide (0.310 g, 2.00 mmol) was added with stirring to an ice-cooled solution of Hpdf (0.830 g, 2.00 mmol) and 1-hydroxybenzotriazole (0.270 g, 2.00 mmol) in dry dichloromethane (50 mL). Stirring was continued for 1 h at 0 °C. The resulting solution was added to a solution of $[-CH_2N(CH_2CH_2C(O)NHCH_2CH_2NH_2)_2]_2$ (0.250 g, 0.48 mmol) in dry dichloromethane (25 mL). The

mixture was stirred at room temperature overnight and then extracted with a NH_4Cl solution, saturated aqueous $KHCO_3$, and brine. The organic phase was dried over $MgSO_4$ and evaporated. The solid residue was purified by column chromatography on alumina eluting first with dichloromethane and then with dichloromethane/ethanol (50:1). Evaporation of the second (major) fraction afforded **P4** as an orange solid foam. Yield: 0.430 g (43%).

^{1}H NMR (DMSO): δ 2.21 (m, 8 H, CH_2), 2.41 (m, 2 H, CH_2), 2.64 (m, 8 H, CH_2), 3.20 (m, 16 H, CH_2), 4.04 (vq, J = 1.9 Hz, 8 H, fc), 4.11 (vt, J = 1.9 Hz, 8 H, fc), 4.35 (vt, J = 1.8 Hz, 8 H, fc), 4.69 (vt, J = 1.9 Hz, 8 H, fc), 7.26–7.37 (m, 40 H, PPh_2), 7.86 (t, $^3J_{HH}$ = 5.6 Hz, 4 H, NH), 8.02 (m, 4 H, NH). $^{13}C\{^1H\}$ NMR (DMSO): δ 33.13 (bs), 38.46 (bs), 38.54 (bs), 49.50 (bs), 50.22 (bs) (5 × CH_2); 68.87, 71.15 (2 × CH of fc); 72.82 (d, J_{PC} = 4 Hz), 73.44 (d, J_{PC} = 15 Hz) (2 × CH of fc); 76.51 (d, $^1J_{PC}$ = 9 Hz, C_{ipso} of fc), 77.13 (C_{ipso} of fc), 128.19 (d, J_{CP} = 6 Hz), 128.52, 132.94 (d, J_{CP} = 20 Hz) (3 × CH of PPh_2); 138.24 (d, $^1J_{PC}$ = 11 Hz, C_{ipso} of PPh_2), 168.48, 171.52 (bs) (2 × C=O). $^{31}P\{^1H\}$ NMR (DMSO): δ −18.1. IR (Nujol): $\tilde{\nu}$/cm^{-1} 3270 (m) (ν_{NH}), 1634 (vs) (amide I), 1539 (vs) (amide II), 1434 (s), 1300 (m), 1192 (w), 1160 (m), 1093 (w), 1069 (w), 1027 (m), 832 (m), 830 (w), 743 (s), 697 (s), 495 (m), 453 (w). ESI ± MS: m/z 2102 ($[M+H]^+$), 2136 ($[M+Cl]^-$). HR MS calcd. for $C_{114}H_{117}{}^{56}Fe_4N_{10}O_8P_4$ ($[M+H]^+$): 2101.5404, found 2101.5388.

4.5. General procedure for the Suzuki cross-coupling reaction

Aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), the appropriate phosphinoamide ligand (an amount corresponding to 1.2 μmol of phosphorus, added as a stock solution in dioxane and diluted up to 1 mL), and 1,2-bis(2-methoxyethoxy)ethane (0.5 mmol) as internal standard were mixed with dioxane (3 mL) under an argon atmosphere. Then, $Pd(OAc)_2$ (1.0 μmol as a stock solution in dioxane and diluted to 1 mL; 0.1 mol%) was added and the mixture was transferred to an oil bath preheated to 100 °C. After stirring for 16 h, the mixture was cooled to room temperature and the conversion determined by ^{1}H NMR spectroscopy.

4.6. Procedures for the Heck reaction

Catalytic tests at 0.1 mol% palladium loading were performed in a three-necked flask (50 mL) equipped with a magnetic stirring bar and rubber septa, immersed in a thermostated oil bath (±2 °C). The reaction mixture was prepared by mixing *n*-butyl acrylate (385 mg, 3.0 mmol), bromobenzene (314 mg, 2.0 mmol), sodium acetate (0.248 g, 3.0 mmol), 1,2-bis(2-methoxyethoxy)ethane as an internal standard (150 mg, 0.85 mmol), solvent DMA (5 mL), palladium acetate (0.46 mg, 2 μmol, 0.1 mol% with respect to bromobenzene) and the ligand **P1** (0.94 mg, 2 μmol), and transferred to an oil bath preheated to 155 °C.

Catalytic tests with 0.5 mol% Pd loading have been performed similarly and at the same temperature with reaction mixtures consisting of *n*-butyl acrylate (192 mg, 1.5 mmol), bromobenzene (157 mg, 1.0 mmol), a base (1.5 mmol), 1,2-bis(2-methoxyethoxy)ethane as an internal standard (100 mg, 0.57 mmol), solvent DMF (5 mL), palladium acetate (1.15 mg, 5 μmmol, 0.5 mol% with respect to bromobenzene), and the ligand in an amount corresponding to a Pd:P molar ratio of 1.2:1.

The composition of the reaction mixture was monitored by withdrawing aliquots that were first centrifuged at 4000 rpm for 10 min to remove the solid components and subsequently analyzed by a high-resolution gas chromatography (Agilent 6850 chromatograph equipped with a flame ionization detector and DB-5 column, 10 m long, 0.1 mm in diameter and 0.1 μm film). The identity of the reaction product was checked by GC–MS measurements (Agilent 5975).

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