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# Amidoamine-based dendrimers with end-grafted Pd–Fe units: Synthesis, characterization and their use in the Heck reaction

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ABSTRACT

The synthesis and characterization of novel amidoamine-based metallodendrimers with heterobimetallic end-grafted amidoferrocenyl-palladium-allyl chloride units is described. Dendrimer $(Fe((\eta^5-C_5H_4PPh_2)(\eta^5-C_5H_4))C(O)HNCH_2CH_2NHC(O)CH_2CH_2)N[CH_2CH_2N(CH_2CH_2C(O)NHCH_2CH_2NH-C(O)(Fe(\eta^5-C_5H_4)(\eta^5-C_5H_4PPh_2)))_2]_2$ (**9-Fe**) and the corresponding metal species $(Fe((\eta^5-C_5H_4PPh_2(Pd(\eta^3-C_3H_5)Cl))(\eta^5-C_5H_4))C(O)HNCH_2CH_2NHC(O)CH_2CH_2)N[CH_2CH_2N(CH_2CH_2C(O)NHCH_2CH_2NHC(O)(Fe(\eta^5-C_5H_4)(\eta^5-C_5H_4PPh_2(Pd(\eta^3-C_3H_5)Cl))))_2]_2$ (**9-Fe–Pd**) were prepared by a consecutive divergent synthesis methodology including addition–amidation cycles, standard peptide coupling, and coordination procedures. For comparative reasons also the monomeric and dimeric molecules $(Fe(\eta^5-C_5H_4PPh_2)(\eta^5-C_5H_4C(O)NH^nC_3H_7))$ (**5-Fe**) and $[Fe(\eta^5-C_5H_4PPh_2)(\eta^5-C_5H_4C(O)NHCH_2)]_2$ (**6-Fe**) as well as $N(CH_2CH_2C(O)NHCH_2CH_2NHC(O)(Fe(\eta^5-C_5H_4)(\eta^5-C_5H_4PPh_2)))_3$ (**7-Fe**) and $[CH_2N(CH_2CH_2C(O)NHCH_2CH_2NHC(O)(Fe(\eta^5-C_5H_4)(\eta^5-C_5H_4PPh_2)))_2]_2$ (**8-Fe**) were prepared from $Fe(\eta^5-C_5H_4PPh_2)(\eta^5-C_5H_4CO_2H)$ (**3**). Using $[Pd(\eta^3-C_3H_5)Cl]_2$ (**4**) as palladium source heterobimetallic metallodendrimers $(Fe(\eta^5-C_5H_4PPh_2(Pd(\eta^3-C_3H_5)Cl))(\eta^5-C_5H_4C(O)NH^nC_3H_7))$ (**5-Fe–Pd**), $[Fe(\eta^5-C_5H_4PPh_2(Pd(\eta^3-C_3H_5)Cl))(\eta^5-C_5H_4C(O)NHCH_2)]_2$ (**6-Fe–Pd**), $N(CH_2CH_2C(O)NHCH_2CH_2NHC(O)(Fe(\eta^5-C_5H_4)(\eta^5-C_5H_4PPh_2(Pd(\eta^3-C_3H_5)Cl))))_3$ (**7-Fe–Pd**) and $[CH_2N(CH_2CH_2C(O)NHCH_2CH_2NHC(O)(Fe(\eta^5-C_5H_4)(\eta^5-C_5H_4PPh_2(Pd(\eta^3-C_3H_5)Cl))))_2]_2$ (**8-Fe–Pd**) were synthesized. Additionally, seleno-phosphines of **5-Fe–Se** and **9-Fe–Se**, respectively, were prepared by addition of elemental selenium to **5-Fe** or **9-Fe** to estimate their $\sigma$-donor properties.

The palladium-containing amidoamine supports are catalytically active in the Heck–Mizoroki cross-coupling of iodobenzene with *tert*-butyl acrylate. The catalytic data are compared to those obtained for the appropriate mononuclear and dinuclear compounds **5-Fe–Pd** and **6-Fe–Pd**. This comparison confirms a positive cooperative effect. The mercury drop test showed that (nano)particles were formed during catalysis, following on heterogeneous carbon–carbon cross-coupling.

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## 1. Introduction

Since the early work of G. van Koten [1] on homogeneous catalysts immobilized on soluble inert silicon-based dendrimer supports there is a rapid development in this field of chemistry recognized which merges heterogeneous and homogeneous catalysis, respectively [2]. Metallodendrimers depending on their size properties take advantage of a simple catalyst separation and recovery [3]. Furthermore, immobilization on a dendrimer support may influence the activity (positive or negative dendritic effect) and/or selectivity of a catalytic reaction, when compared with their monomeric analogs. In addition to silicon-containing dendritic frameworks, amidoamine dendrimers with their nitrogen and amide functionalities give advantage as high capacity chelating molecules for the stabilization of catalytic active species during the catalytic process [4]. So far, dendrimers with peripherally attached mononuclear organometallic or metal-organic chiral and *non*-chiral units including nickel [5], palladium [6,7], platinum [8], cobalt [9], rhodium [10,11] and ruthenium [12] fragments have been applied in a variety of homogeneous catalyses. In this context, the utilization of ferrocenyl phosphine functionalized supports in combination with diverse palladium sources to *in-situ* generate catalytic active species in carbon–carbon cross coupling reactions has widely been described [13]. About the use of individual heterobimetallic end-grafted organometallics featuring at least one catalytic active transition metal atom has to the best of our knowledge not been reported in dendrimer chemistry so far, however, very recently a method was reported to prepare the PAMAM-based dendrimer G4OH-$(Pt^{2+})_x(Ru^{3+})_y$ by subsequent addition of $K_2[PtCl_4]$ and $[RuCl_3]$, respectively, to dendrimer G4OH

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in an aqueous solution [14]. Nevertheless, the proposed heterobimetallic Pt–Ru complexes were not isolated.

With this in mind and as a continuation of our research in the field of dendrimers [15] and carbon–carbon cross-coupling reactions [16], we here describe the immobilization of catalytic active palladium ferrocenyl phosphines using amidoamine dendrimers. The use of the appropriate supported heterobimetallic Fe–Pd systems as catalysts in the Heck–Mizoroki [17–19] (reaction of iodobenzene with *tert*-butyl acrylate) reaction is reported.

## 2. Results and discussion

### 2.1. Synthesis of amidoamine dendrimers

Amidoamine dendrimers were prepared by a divergent consecutive synthesis procedure firstly described by Tomalia and coworkers [20]. This synthesis methodology was applied to the preparation of **2** as depicted in Scheme 1. After appropriate work-up, this dendrimer with its five terminal amino functionalities could be isolated as a colorless oil in almost quantitative yield (Section 4).

Dendrimer **2** was characterized by elemental analysis, IR and NMR ($^1$H, $^{13}$C{$^1$H}) spectroscopy. As for related amidoamine compounds [21a] the NMR spectroscopic characterization of **2** revealed single resonance patterns for the $C(O)CH_2CH_2$, $C(O)CH_2$, $HNCH_2$, $CH_2NH_2$ and $NH_2$ fragments of which, as expected, the latter group appears as a broad signal (Section 4). Most characteristic in the IR spectrum of **2** is the observation of three very distinctive absorptions at 3365 ($\nu_{NH}$), 1640 ($\nu_{C(O)}$, amide I), and 1560 cm$^{-1}$ ($\nu_{C(O)}$, amide II) (Section 4).

### 2.2. Synthesis of metallo and selenium–phosphine amidoamine dendrimers

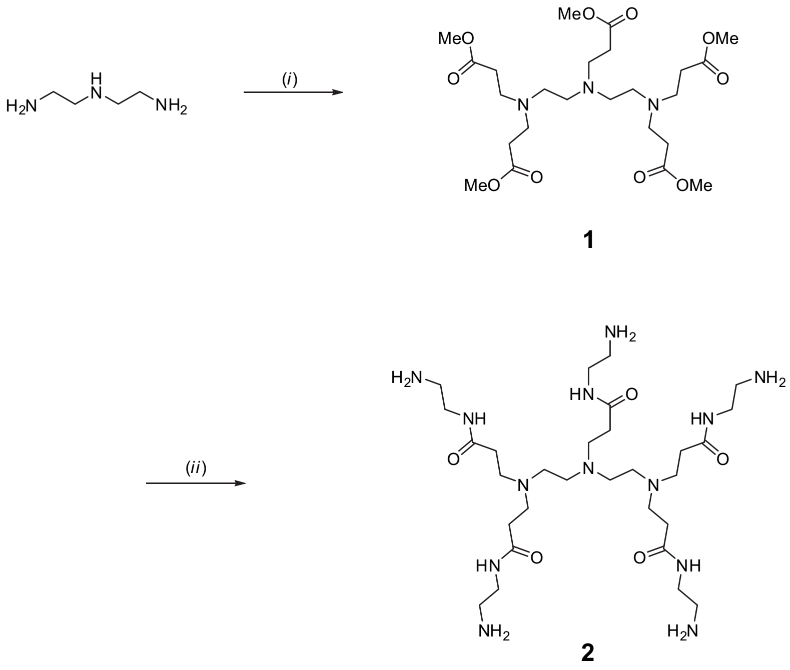
The iron–palladium organometallic moieties were attached to the dendrimer periphery *via* peptide coupling by treatment of (diphenylphosphino)ferrocenyl carboxylic acid (**3**) [21b] with the $NH_2$-functionalized amidoamine support (**2**) under standard peptide coupling conditions in presence of HOBT (=*h*ydr*o*xy*b*enzo*t*riazole) and EDC (=1-*e*thyl-3-(3-*d*imethylamino-propyl)carbodiimide), respectively, which was further reacted with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (**4**) [21c] to give heterobimetallic **9-Fe–Pd** (Scheme 2). Organometallic **9-Fe–Pd** was obtained in an overall yield of 26 % (Section 4). For comparison, the organometallic molecules **5-Fe–Pd** to **8-Fe–Pd** were synthesized in a consecutive reaction sequence using the same reaction conditions as described for the synthesis of **9-Fe–Pd** (Fig. 1).

Compounds **9-Fe** and **5-Fe–Pd** to **9-Fe–Pd** are odorless, stable to air and moisture, dissolve in polar organic solvents, *e.g.* in dichloromethane and tetrahydrofuran, while being poorly soluble in benzene and toluene. Dendrimer **9-Fe** featuring as terminal group the ferrocenyl diphenylphosphine is an orange colored solid, whereas the defined coordination compounds Fe–Pd (**5-Fe–Pd** to **9-Fe–Pd**) are bright yellow.

All ferrocenyl and heterobimetallic Fe–Pd metallodendrimers **9-Fe** and **5-Fe–Pd** to **9-Fe–Pd** gave correct elemental analyses. As the unimolecular amidoamine molecule **2**, the appropriate metallodendrimer **9-Fe–Pd** shows separated and well-resolved signals with the expected coupling pattern in the NMR spectra (Section 4).

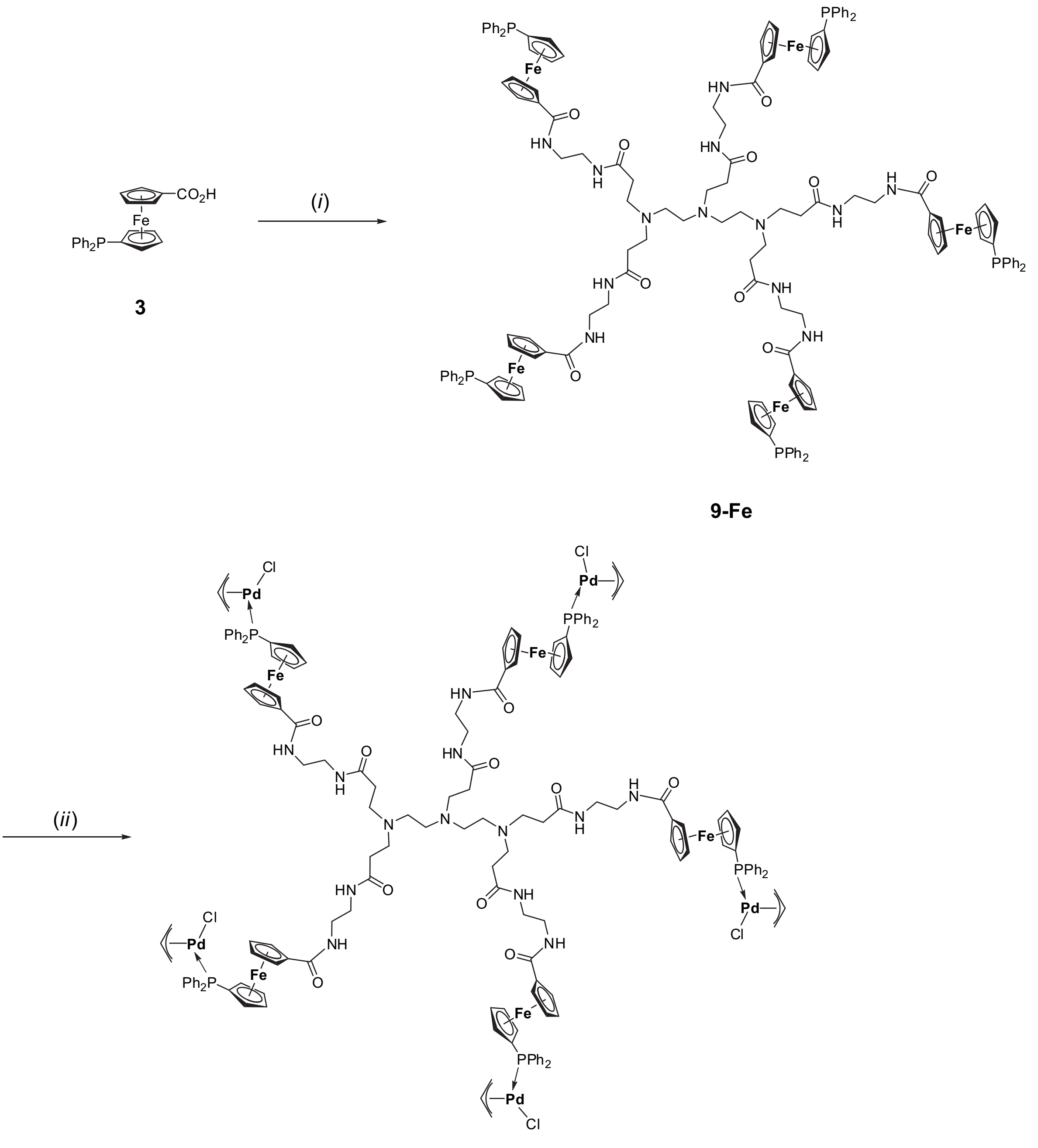
The successful attaching of **3** to the amidoamine scaffold **2** can nicely be proofed by IR and NMR spectroscopy. In IR spectroscopy the absorption at ca. 1670 ($\nu_{C(O)}$) disappears, proofing complete consumption of the carboxylic acid (**3**). The formation of the amide connectivity can best be figured with $^1$H NMR spectroscopy. For example, the signal of the terminal $NH_2$ moiety is shifted to lower field at 7.82 ppm in course of the reaction [21a]. In the $^{13}$C{$^1$H} NMR spectra the resonance of the carbonyl carbon atom of the carboxylic acid (**3**) is shifted from 177 to ca. 170 ppm [21b] (Section 4).

The presence of a diphenylphosphine ferrocenyl sandwich unit in **9-Fe** is discernable by the appearance of a singlet at −17.9 ppm in the $^{31}$P{$^1$H} NMR (Section 4). Through coordination of the phosphorus atom to palladium as given in heterobimetallic compound **9-Fe–Pd** a representative shift to lower field occurs (13.3 ppm). The chemical



(($i$) $CH_2CHCO_2Me$, methanol, 25 °C, 72 hrs; ($ii$) $H_2NCH_2CH_2NH_2$, methanol, 25 °C, 72 hrs).

**Scheme 1.** Synthesis of amidoamine dendrimer **2**.



3

9-Fe

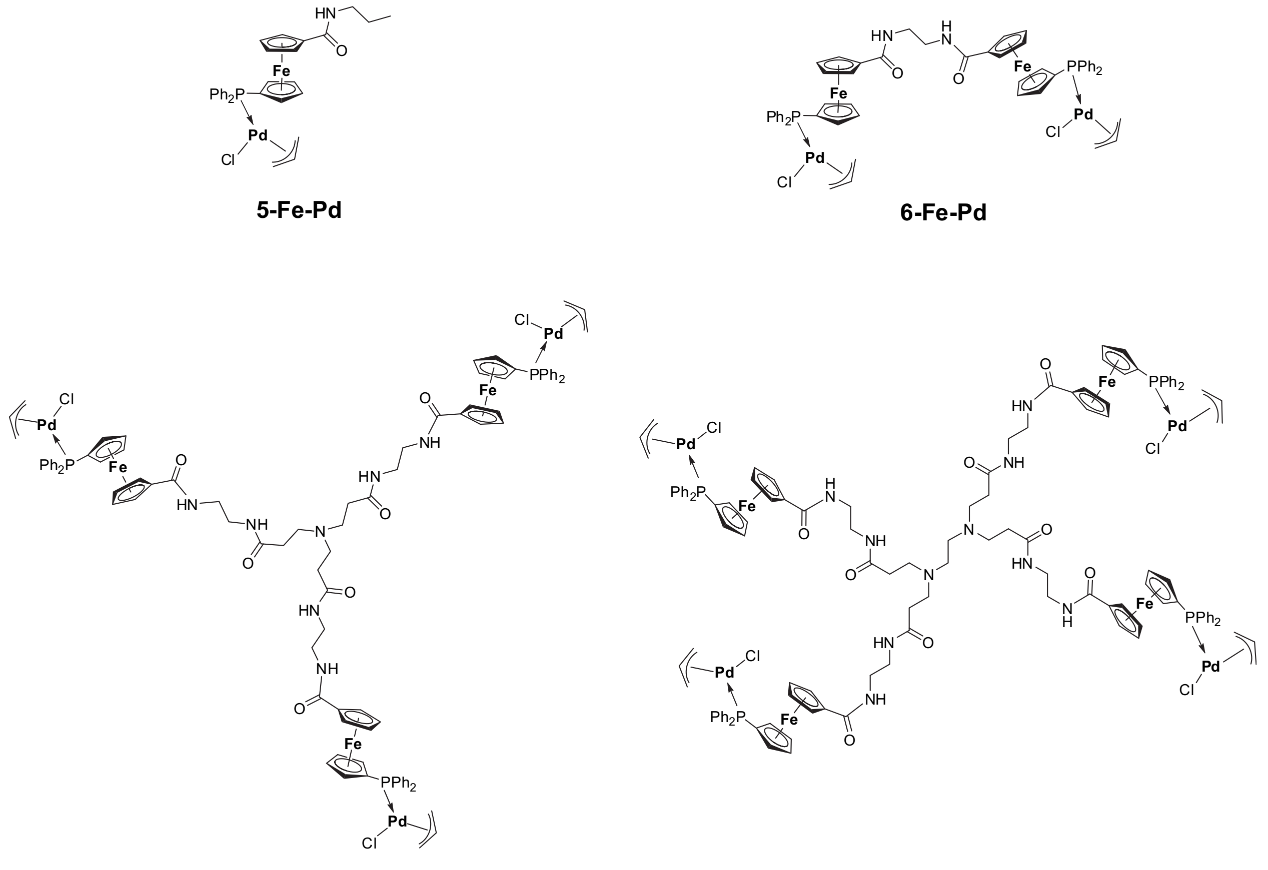
9-Fe-Pd

((*i*) **2**, HOBT (= *h*ydr*o*xy*b*enzo*t*riazole), EDC (= 1-*e*thyl-3-(3-*d*imethylaminopropyl)-*c*arbodiimide, dichloromethane, 0 → 25 °C, 12 hrs; (*ii*) [Pd($\eta^3$-$C_3H_5$)Cl]$_2$ (**4**), dichloromethane, 25 °C, 1 h).

**Scheme 2.** Synthesis of heterobimetallic **9-Fe–Pd**.

shift of the datively bonded $Ph_2P$ group is, as expected, almost independent of the appropriate amidoamine scaffold [22]. The newly introduced [Pd($\eta^3$-$C_3H_5$)Cl] organometallic fragment in **5-Fe–Pd** to **9-Fe–Pd** can also be recognized in the $^1H$ and $^{13}C\{^1H\}$ NMR spectra. In the $^1H$ NMR spectra the allyl moieties give rise to three distinctive resonances at ca. 2.8 (CH-*anti*), 3.8 (CH-*syn*), and 5.5 ppm (CH-*centered*) as a result of the different chemical environment within the allyl unit, while in $^{13}C\{^1H\}$ spectroscopy two signals can be assigned at ca. 62 ($CH_2$) and 118 ppm (CH) (Section 4) [23].

The $\sigma$-donor properties of phosphines can be quantified by the phosphorus–selenium coupling constant $^1J_{(^{31}P-^{77}Se)}$ of the appropriate seleno derivatives [24]. Therefore, we reacted the phosphino ferrocenyl amidoamines **9-Fe** and **5-Fe** with selenium in dichloromethane at ambient temperature to obtain the appropriate



**5-Fe-Pd** **6-Fe-Pd** **7-Fe-Pd** **8-Fe-Pd**

**Fig. 1.** Heterobimetallic amidoamines **5-Fe**–**Pd** to **8-Fe**–**Pd**.

seleno-phosphine derivatives **9-Fe**–**Se** and **5-Fe**–**Se** (Fig. 2) to classify the electronic properties of the immobilized phosphino ferrocenes and range them with conventionally phosphines. After appropriate work-up, **5-Fe**–**Se** and **9-Fe**–**Se** were isolated as orange solids in almost quantitative yield (Section 4).

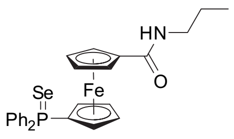
The phosphorus–selenium coupling constants of **5-Fe**–**Se** and **9-Fe**–**Se** were determined to $^{1}J_{(^{31}P-^{77}Se)} = 720$ Hz (**5-Fe**–**Se**) and 723 Hz (**9-Fe**–**Se**), being slightly decreased, when compared with $FcPh_2P=Se$ $^{1}J_{(^{31}P-^{77}Se)} = 731$ Hz) and $Ph_3P=Se$ ($^{1}J_{(^{31}P-^{77}Se)} =$ 729 Hz) [25]. Obviously, the immobilization on the scaffold has no negative impact on the $\sigma$-donor properties of the phosphines. Furthermore, the phosphorus–selenium coupling constants indicate no influence according to the number of the immobilized diphenylphosphino ferrocenyl fragments.

### *2.3. Catalysis with heterobimetallic iron–palladium amidoamine dendrimers*

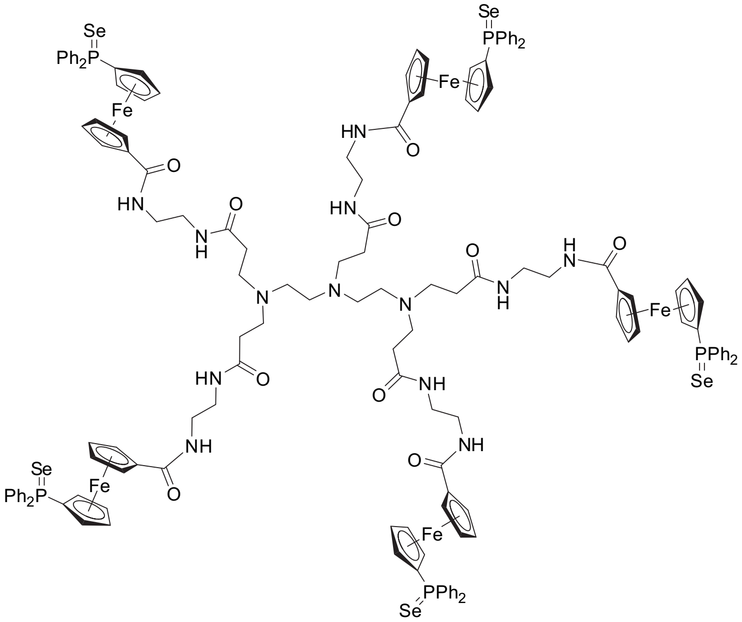
To enrich the family of existing Heck catalysts, we applied the above described heterobimetallic Fe–Pd phosphines **5-Fe**–**Pd** to **9-Fe**–**Pd** in vinylation reactions, as metal-containing phosphines and particularly those based on a ferrocene scaffold have played a very important role in many organic transformations catalyzed by palladium complexes [26]. In comparative studies these newly synthesized compounds showed to be efficient catalysts in the carbon–carbon cross coupling of iodobenzene with *tert*-butyl acrylate. The results obtained for dendrimers **6-Fe**–**Pd** to **9-Fe**–**Pd** are compared with the parent model **5-Fe**–**Pd** and are comparatively discussed in terms of the potential ability of the amidoamine scaffold stabilizing catalytic active palladium species. The homogeneous palladium-catalyzed vinylation was performed as described by Boys and Butler [27]. Thus, the appropriate organic coupling reagents (3.0 mmol iodobenzene (**10**), 3.1 mmol *tert*-butyl acrylate (**11**)) were reacted in a toluene-acetonitrile mixture of ratio 1:1 ($v/v$), in the presence of $NEt^{i}Pr_2$ (3.1 mmol) as a base, [CuI] (two equivalents) as reducing reagent [27], and a (pre)catalyst loading of 0.5 mol% of palladium at a comparative mild reaction temperature (80 °C) (Reaction 1, Fig. 3, Table 1, Section 4). The initial reaction rate, conversion, TON (=*t*urn-*o*ver-*n*umber), and TOF (=*t*urn-*o*ver-*f*requency) data are reported.

From Fig. 3 and Table 1 it can be seen that the best productivity is reached with catalyst **9-Fe**–**Pd** possessing the highest number of terminal heterobimetallic Fe–Pd-units. It can also be recognized that there is a positive synergistic effect most pronounced between **5-Fe**–**Pd**/**6-Fe**–**Pd**, **7-Fe**–**Pd**/**8-Fe**–**Pd**, and **9-Fe**–**Pd** (Fig. 3). As the electronic properties of all the compounds are similar ($^{1}J_{(^{31}P-^{77}Se)}$, vide supra), the different catalytic activity is most likely caused by cooperative effects between the catalytic active palladium species formed and the amino groups of the amidoamine scaffold. The higher the number of terminal metal fragments and of intrinsic amino units, the higher is the catalytic activity for the embedded palladium catalyst. Similar results of a positive "dendritic effect" on chemical yields, which means that the activity is improved by increasing the number of terminal metal-containing groups, have been reported recently [3c,16e,28,29]. For all heterobimetallic Fe–Pd systems concomitant precipitation of metallic palladium occurs during the catalytic reaction, which decreases in the series **5-Fe**–**Pd**/**6-Fe**–**Pd** > **7-Fe**–**Pd**/**8-Fe**–**Pd** > **9-Fe**–**Pd**.

By means of the Hg(0) drop test, reaction mixtures of iodobenzene (**10**), *tert*-butyl acrylate (**11**) and 0.5 mol% of **8-Fe**–**Pd** as



**5-Fe-Se**



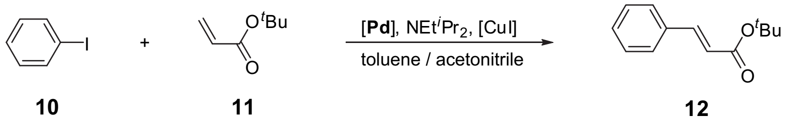
**9-Fe-Se**

**Fig. 2.** Seleno-phosphines **5-Fe–Se** and **9-Fe–Se**.

(pre)catalyst are quenched with metallic mercury (Fig. 4) at certain times [30]. Quenching after the catalytically active system is formed ($t = 45$ min) extinguishes the catalytic activity instantly, while adding mercury at the beginning of the catalysis ($t = 0$ min) even prevents the formation of a catalytic active palladium species. This observations of poisoning implies heterogeneous Heck–Mizoroki reactions promoted by Pd(0) particles [31].

## 3. Conclusions

The preparation and characterization of defined Fe–Pd phosphine functionalized amidoamines $N(CH_2CH_2C(O)NHCH_2CH_2NHC(O)(Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_4PPh_2(Pd(\eta^3\text{-}C_3H_5)Cl))))_3$, $[CH_2N(CH_2CH_2C(O)NHCH_2CH_2NHC(O)(Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_4PPh_2(Pd(\eta^3\text{-}C_3H_5)Cl))))_2]_2$, $(Fe((\eta^5\text{-}C_5H_4PPh_2(Pd(\eta^3\text{-}C_3H_5)Cl))(\eta^5\text{-}C_5H_4))C(O)HNCH_2CH_2NHC(O)$



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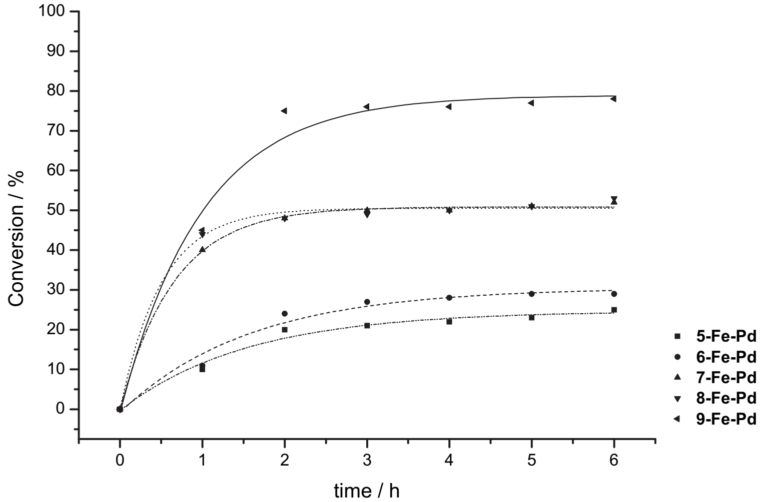

**Fig. 3.** Kinetic investigation of **5-Fe–Pd** to **9-Fe–Pd** in the Heck–Mizoroki carbon–carbon cross-coupling reaction of iodobenzene (**10**) with *tert*-butyl acrylate (**11**) to give *E-tert*-butyl cinnamate (**12**) (0.5 mol% (pre)catalyst; conversion time 0–6 h).

**Table 1**
Results of the Heck–Mizoroki C–C cross-coupling of iodobenzene with *tert*-butyl acrylate by **5-Fe–Pd** to **9-Fe–Pd**.

| Compd. | **5-Fe–Pd** | **6-Fe–Pd** | **7-Fe–Pd** | **8-Fe–Pd** | **9-Fe–Pd** |
|---|---|---|---|---|---|
| Yield of **12** [%][a] | 44 | 48 | 61 | 63 | 88 |
| TON[b] | 88 | 96 | 122 | 126 | 176 |
| TOF [1/h][c] | 20 | 24 | 80 | 88 | 90 |

[a] Yields are determined by $^1H$ NMR spectroscopy with acetylferrocene as standard relative to *E*-*tert*-butyl cinnamate (**12**), reaction time 24 h.

[b] Mol product/mol [Pd].

[c] Mol product/mol [Pd]/2, determined after 1 h.

$CH_2CH_2)N[CH_2CH_2N(CH_2CH_2C(O)NHCH_2CH_2NHC(O)(Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_4PPh_2(Pd(\eta^3\text{-}C_3H_5)Cl))))_2]_2$, $(Fe(\eta^5\text{-}C_5H_4PPh_2(Pd(\eta^3\text{-}C_3H_5)Cl))(\eta^5\text{-}C_5H_4C(O)NH^nC_3H_7))$, and $[Fe(\eta^5\text{-}C_5H_4PPh_2(Pd(\eta^3\text{-}C_3H_5)Cl))(\eta^5\text{-}C_5H_4C(O)NHCH_2)]_2$, for comparison, using consecutive divergent growth methodologies including addition, amidation, and complexation reactions is described. These molecules are unique because they feature as end-grafted moieties heterobimetallic ferrocenyl-based palladium allyl chlorides. These individual metallodendrimers were successfully employed as homogeneous Heck catalysts in the vinylation of iodobenzene with *tert*-butyl acrylate to give *E-tert*-butyl cinnamate. The newly prepared Fe–Pd-catalysts are less active than the catalyst systems reported earlier with any combination of *N*-heterocyclic carbenes [32], bulky electron-rich chelating bis(phosphines) [33], palladacycles [34], secondary phosphates or phosphonium salts [29a,35], however, the systems prepared show synergistic and cooperative effects resulting in higher yields and productivities with increasing numbers of end-grafted Fe–Pd phosphine moieties. Due to the larger organic matrix with its specific, intrinsic amine functionalities the amidoamine scaffold with the most immobilized heterobimetallic iron–palladium features is best suited for the stabilization of the catalytic active species.

## 4. Experimental

### 4.1. Materials and methods

Syntheses were performed under a dry and deoxygenated dinitrogen atmosphere using standard Schlenk techniques unless otherwise stated. All solvents were carefully dried by standard procedures over the appropriate drying agents and distilled immediately prior to use. The reagents that where purchased commercially were used without further purification. (Diphenylphosphino)ferrocenyl carboxylic acid (**3**) [21b], $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (**4**) [21c] and **5-Fe** to **8-Fe** [16e] were prepared according to published procedures.

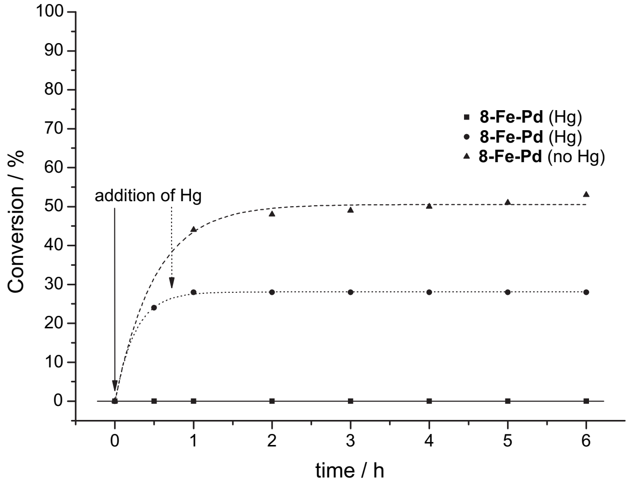

**Fig. 4.** Hg(0) drop tests of **8-Fe–Pd** in the Heck–Mizoroki reactions by addition of metallic mercury at certain times ($t = 0$ min; $t = 45$ min) and without the addition of mercury for comparison.

$^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded with a Bruker Avance III 500 MHz spectrometer. Chemical shifts $\delta$ are given in ppm (parts per million) using the particular solvent or $H_3PO_4$ as external standard as reference signal. Coupling constants $J$ are given in Hertz (Hz). IR spectra were recorded with a FT Nicolet IR 200 instrument in the range of 500–4000 $cm^{-1}$. The melting points were obtained using capillaries with an electro thermal melting point apparatus. Microanalyses were performed with a C, H, N-analyzer FLASHEA 1112 Series (Thermo Inc.).

### 4.2. *Preparation of* $H_2NCH_2CH_2NHC(O)CH_2CH_2N(CH_2CH_2N(CH_2CH_2C(O)NHCH_2CH_2NH_2)_2)_2$ (**2**)

Poly(amidoamine)dendrimer **2** was synthesized by a preparation procedure firstly described by Tomalia et al. [21a], in a two step synthesis methodology using 1.0 g (9.7 mmol) of diethylenetriamine in 20 mL of methanol. After subsequent addition of methyl acrylate (10 g, 116 mmol) at 25 °C an excess of ethylenediamine (33.5 mL, 0.5 mol) was added in a single portion. After 3 days of stirring all volatiles were evaporated in oil-pump vacuum, whereby **2** was obtained as colorless oil (6.5 g, 99 %, based on diethylenetriamine). Anal. Calc for $C_{29}H_{63}N_{13}O_5$ (673.9): C, 51.69; H, 9.42; N, 27.02. Found: C, 52.03; H, 9.67; N, 27.19. $^1H$ NMR ($\delta$, $CDCl_3$): 1.45 (bs, 10 H, $NH_2$), 2.37 (m, 10 H, $CH_2C(O)$), 2.56 (br, 8 H, $NCH_2CH_2N$), 2.74 (t, 10 H, $^3J_{HH} = 6.9$ Hz, $NCH_2CH_2C(O)$), 2.78 (t, 10 H, $^3J_{HH} = 6.3$ Hz, $CH_2NH_2$), 3.25 (t, 10 H, $^3J_{HH} = 6.3$ Hz, $NHCH_2$), 7.66 (m, 5 H, $C(O)NH$). $^{13}C\{^1H\}$ NMR ($\delta$, $CDCl_3$): 32.1 ($CH_2C(O)$), 41.3 ($NHCH_2$), 42.3 ($CH_2NH_2$), 51.4 ($NCH_2CH_2N$), 52.0 ($NCH_2CH_2N$), 54.2 ($NCH_2CH_2C(O)$), 168.4 ($C(O)$). IR (NaCl, $cm^{-1}$): 3365 (vs, $\nu_{NH2}$), 1640 (vs, $\nu_{C(O)}$, amide I), 1560 (s, $\nu_{C(O)}$, amide II).

### 4.3. *Preparation of* $((Fe(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_4))C(O)HNCH_2CH_2NHC(O)CH_2CH_2)N[CH_2CH_2N(CH_2CH_2C(O)NHCH_2CH_2NHC(O)(Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_4PPh_2)))_2]_2$ (**9-Fe**)

300 mg (0.45 mmol) of **2** in 20 mL of dichloromethane were mixed with 950 mg (2.3 mmol) of (diphenylphosphino)ferrocenyl carboxylic acid (**3**) and 310 mg (2.3 mmol) of HOBT. After stirring for 1 h at 0 °C, 355 mg (2.3 mmol) of EDC in 30 mL of dichloromethane was slowly added. The resulting reaction mixture was stirred overnight at 25 °C and afterwards was subsequently washed with 20 mL of an aqueous solution of ammonium chloride (0.5 M). After drying the organic layer over $MgSO_4$ the solvents were removed under reduced pressure. The crude product was purified by column chromatography (column size: 10 × 3 cm, alumina) using dichloromethane as eluent. After evaporation of all volatiles in oil-pump vacuum molecule **9-Fe** was obtained as an air stable, orange colored solid (350 mg, 30 %, based on **2**). Mp: 125 °C. Anal. Calc for $C_{144}H_{148}Fe_5N_{13}O_{10}P_5$ (2654.9): C, 65.15; H, 5.62; N, 6.86. Found: C, 64.63; H, 5.23; N, 6.39. $^1H$ NMR ($\delta$, $CDCl_3$): 2.09 (bs, 20 H, $NCH_2CH_2C(O)$), 2.51 (m, 8 H, $NCH_2CH_2N$), 3.31 (m, 20 H, $HNCH_2CH_2NH$), 4.00 (m, 10 H, $H_\alpha/C_5H_4PPh_2$), 4.07 (m, 10 H, $H_\beta/C_5H_4C(O)$), 4.29 (m, 10 H, $H_\beta/C_5H_4PPh_2$), 4.64 (m, 10 H, $H_\alpha/C_5H_4C(O)$), 7.18–7.31 (m, 50 H, $C_6H_5$), 7.82 (m, 10 H, $NH$). $^{13}C\{^1H\}$ NMR ($\delta$, $CDCl_3$): 29.7 ($CH_2C(O)$), 39.3 ($HNCH_2CH_2NH$), 40.4 ($HNCH_2CH_2NH$), 50.9 ($NCH_2CH_2C(O)$), 51.6 ($NCH_2CH_2N$), 51.9 ($NCH_2CH_2N$), 69.5 ($C_\alpha/C_5H_4C(O)$), 71.9 ($C_\beta/C_5H_4C(O)$), 73.1 (d, $^3J_{CP} = 3$ Hz, $C_\beta/C_5H_4C(PPh_2)$), 74.4 (d, $^2J_{CP} = 13$ Hz, $C_\alpha/C_5H_4C(PPh_2)$), 76.6 ($C_i/C_5H_4C(O)$), 77.5 (d, $^1J_{CP} = 8$ Hz, $C_i/C_5H_4C(PPh_2)$), 128.4 (d, $^3J_{CP} = 6$ Hz, $C_m/C_6H_5$), 128.8 ($C_p/C_6H_5$), 133.5 (d, $^2J_{CP} = 19$ Hz, $C_o/C_6H_5$), 138.5 (d, $^1J_{CP} = 10$ Hz, $C_i/C_6H_5$), 170.9 ($C(O)$), 173.6 ($C(O)$). $^{31}P\{^1H\}$ NMR ($\delta$, $CDCl_3$): −17.9 ($PPh_2$). IR (KBr, $cm^{-1}$): 3300 (m, $\nu_{NH}$), 1640 (s, $\nu_{C(O)}$, amide I), 1540 (s, $\nu_{C(O)}$, amide II).

### *4.4. Preparation of $(Fe(\eta^5\text{-}C_5H_4PPh_2(Pd(\eta^3\text{-}C_3H_5)Cl))(\eta^5\text{-}C_5H_4C(O)NH^nC_3H_7))$ (**5-Fe–Pd**)*

180 mg (0.4 mmol) of $(Fe(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_4C(O)NH^nC_3H_7))$ (**5-Fe**) were dissolved in dichloromethane (20 mL) and 75 mg (0.21 mmol) of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (**4**) were added in a single portion. After 1 h of stirring at 25 °C, **5-Fe–Pd** was purified by precipitation from dichloromethane (5 mL) by addition of 20 mL of *n*-hexane. The precipitate was washed twice with 10 mL portions of *n*-hexane. After appropriate work-up, the title compound was isolated as a bright yellow solid (230 mg, 90 %, based on **5-Fe**). Mp: 150 °C. Anal. Calc for $C_{29}H_{31}ClFeNOPPd$ (638.3): C, 54.57; H, 4.90; N, 2.91. Found: C, 54.44; H, 5.12; N, 2.99. $^1$H NMR ($\delta$, $CDCl_3$): 0.96 (t, 3 H, $^3J_{HH}$ = 7.4 Hz, $CH_3$), 1.65 (m, 2 H, $CH_2CH_2CH_3$), 2.85 (m, 1H, C*H*-*anti*), 3.30 (m, 2 H, $CH_2CH_2CH_3$), 3.78 (m, 1 H, C*H*-*syn*), 4.26 (m, 2 H, $H_\alpha/C_5H_4PPh_2$), 4.57 (m, 2 H, $H_\beta/C_5H_4C(O)$), 5.02 (m, 2 H, $H_\beta/C_5H_4PPh_2$), 5.15 (m, 2 H, $H_\alpha/C_5H_4C(O)$), 5.55 (m, 1 H, C*H*-*centered*), 7.18 (m, 1 H, N*H*), 7.31–7.78 (m, 10 H, $C_6H_5$). $^{13}$C{$^1$H} NMR ($\delta$, $CDCl_3$): 11.7 ($CH_3$), 23.2 ($CH_2CH_2CH_3$), 41.5 ($CH_2CH_2CH_3$), 61.9 ($CH_2$-*syn*/*anti*), 70.3 ($C_\alpha/C_5H_4C(O)$), 71.9 ($C_\beta/C_5H_4C(O)$), 73.5 (d, $^3J_{CP}$ = 5 Hz, $C_\beta/C_5H_4C(PPh_2)$), 74.3 (d, $^1J_{CP}$ = 47 Hz, $C_i/C_5H_4C(PPh_2)$), 76.4 (d, $^2J_{CP}$ = 16 Hz, $C_\alpha/C_5H_4C(PPh_2)$), 78.5 ($C_i/C_5H_4C(O)$), 118.2 (C*H*-*centered*), 128.5 (d, $^3J_{CP}$ = 6 Hz, $C_m/C_6H_5$), 130.2 ($C_p/C_6H_5$), 133.1 (d, $^2J_{CP}$ = 12 Hz, $C_o/C_6H_5$), 135.9 (d, $^1J_{CP}$ = 44 Hz, $C_i/C_6H_5$), 169.2 (*C*(O)). $^{31}$P{$^1$H} NMR ($\delta$, $CDCl_3$): 11.6 (*P*Ph$_2$). IR (KBr, cm$^{-1}$): 3315 (m, $\nu_{NH}$), 1645 (s, $\nu_{C(O)}$, amide I), 1540 (s, $\nu_{C(O)}$, amide II), 1480 (w, $\nu_{\eta^3\text{-}C_3H_5}$).

### *4.5. Preparation of $[Fe(\eta^5\text{-}C_5H_4PPh_2(Pd(\eta^3\text{-}C_3H_5)Cl)))(\eta^5\text{-}C_5H_4C(O))NHCH_2)]_2$ (**6-Fe–Pd**)*

Compound **6-Fe–Pd** was synthesized in the same manner as **5-Fe–Pd**, whereby 150 mg (0.18 mmol) of $[Fe(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_4C(O)NHCH_2)]_2$ (**6-Fe**) were reacted with 70 mg (0.2 mmol) of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (**4**). After appropriate work-up, **6-Fe–Pd** was obtained as a bright yellow solid (200 mg, 92 %, based on **6-Fe**). Mp: 160 °C. Anal. Calc for $C_{54}H_{52}Cl_2Fe_2N_2O_2P_2Pd_2$ (1218.4): C, 53.23; H, 4.30; N, 2.30. Found: C, 53.46; H, 4.31; N, 2.20. $^1$H NMR ($\delta$, $CDCl_3$): 2.67 (m, 2H, C*H*-*anti*), 3.59 (m, 4 H, $CH_2$), 3.86 (m, 2 H, C*H*-*syn*), 4.03 (m, 4 H, $H_\alpha/C_5H_4PPh_2$), 4.27 (m, 4 H, $H_\beta/C_5H_4C(O)$), 4.44 (m, 4 H, $H_\beta/C_5H_4PPh_2$), 4.80 (m, 4 H, $H_\alpha/C_5H_4C(O)$), 5.68 (m, 2 H, C*H*-*centered*), 7.12 (m, 2 H, N*H*), 7.38–7.71 (m, 20 H, $C_6H_5$). $^{13}$C{$^1$H} NMR ($\delta$, $CDCl_3$): 40.6 ($CH_2$), 61.7 ($CH_2$-*syn*/*anti*), 70.2 ($C_\alpha/C_5H_4C(O)$), 72.6 ($C_\beta/C_5H_4C(O)$), 73.7 (d, $^3J_{CP}$ = 9 Hz, $C_\beta/C_5H_4C(PPh_2)$), 74.5 (d, $^1J_{CP}$ = 44 Hz, $C_i/C_5H_4C(PPh_2)$), 76.4 (d, $^2J_{CP}$ = 14 Hz, $C_\alpha/C_5H_4C(PPh_2)$), 77.5 ($C_i/C_5H_4C(O)$), 118.3 (C*H*-*centered*), 128.6 (d, $^3J_{CP}$ = 9 Hz, $C_m/C_6H_5$), 130.3 ($C_p/C_6H_5$), 133.2 (d, $^2J_{CP}$ = 12 Hz, $C_o/C_6H_5$), 135.4 (d, $^1J_{CP}$ = 44 Hz, $C_i/C_6H_5$), 170.7 (*C*(O)). $^{31}$P{$^1$H} NMR ($\delta$, $CDCl_3$): 11.4 (*P*Ph$_2$). IR (KBr, cm$^{-1}$): 3315 (m, $\nu_{NH}$), 1640 (s, $\nu_{C(O)}$, amide I), 1535 (s, $\nu_{C(O)}$, amide II), 1485 (w, $\nu_{\eta^3\text{-}C_3H_5}$).

### *4.6. Preparation of $N(CH_2CH_2C(O)NHCH_2CH_2NHC(O)(Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_4PPh_2(Pd(\eta^3\text{-}C_3H_5)Cl))))_3$ (**7-Fe–Pd**)*

Compound **7-Fe–Pd** was synthesized in the same way as **5-Fe–Pd**, whereby 140 mg (0.09 mmol) of $N(CH_2CH_2C(O)NHCH_2CH_2NHC(O)(Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_4PPh_2)))_3$ (**7-Fe**) were reacted with 50 mg (0.135 mmol) of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (**4**). After appropriate work-up, **7-Fe–Pd** was obtained as a bright yellow solid (165 mg, 88 %, based on **7-Fe**). Mp: 165 °C. Anal. Calc for $C_{93}H_{99}Cl_3Fe_3N_7O_6P_3Pd_3$ (2096.9): C, 53.27; H, 4.76; N, 4.68. Found: C, 53.13; H, 4.91; N, 4.52. $^1$H NMR ($\delta$, $CDCl_3$): 2.37 (m, 6 H, $CH_2C(O)$), 2.72 (m, 6 H, $NCH_2CH_2C(O)$), 2.97 (m, 3 H, C*H*-*anti*), 3.43 (bs, 12 H, $HNCH_2CH_2NH$), 3.84 (m, 3 H, C*H*-*syn*), 4.01 (m, 6 H, $H_\alpha/C_5H_4PPh_2$), 4.29 (m, 6 H, $H_\beta/C_5H_4C(O)$), 4.53 (m, 6 H, $H_\beta/C_5H_4PPh_2$), 4.99 (m, 6 H, $H_\alpha/C_5H_4C(O)$), 5.64 (m, 3 H, C*H*-*centered*), 7.29–7.81 (m, 30 H, $C_6H_5$), 7.87 (m, 6 H, N*H*). $^{13}$C{$^1$H} NMR ($\delta$, $CDCl_3$): 29.9 ($NCH_2CH_2C(O)$), 39.6 ($HNCH_2CH_2NH$), 39.9 ($HNCH_2CH_2NH$), 50.0 ($NCH_2CH_2C(O)$), 59.9 ($CH_2$-*syn*/*anti*), 69.9 ($C_\alpha/C_5H_4C(O)$), 72.4 ($C_\beta/C_5H_4C(O)$), 73.6 (d, $^3J_{CP}$ = 7 Hz, $C_\beta/C_5H_4C(PPh_2)$), 73.9 (d, $^1J_{CP}$ = 43 Hz, $C_i/C_5H_4C(PPh_2)$), 74.5 (d, $^2J_{CP}$ = 15 Hz, $C_\alpha/C_5H_4C(PPh_2)$), 77.5 ($C_i/C_5H_4C(O)$), 118.4 (C*H*-*centered*), 128.3 (d, $^3J_{CP}$ = 10 Hz, $C_m/C_6H_5$), 130.3 ($C_p/C_6H_5$), 132.7 (d, $^2J_{CP}$ = 12 Hz, $C_o/C_6H_5$), 135.6 (d, $^1J_{CP}$ = 42 Hz, $C_i/C_6H_5$), 170.6 (*C*(O)), 171.9 (*C*(O)). $^{31}$P{$^1$H} NMR ($\delta$, $CDCl_3$): 12.5 (*P*Ph$_2$). IR (KBr, cm$^{-1}$): 3300 (m, $\nu_{NH}$), 1640 (s, $\nu_{C(O)}$, amide I), 1540 (s, $\nu_{C(O)}$, amide II), 1480 (w, $\nu_{\eta^3\text{-}C_3H_5}$).

### *4.7. Preparation of $[CH_2N(CH_2CH_2C(O)NHCH_2CH_2NHC(O)(Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_4PPh_2(Pd(\eta^3\text{-}C_3H_5)Cl))))_2]_2$ (**8-Fe–Pd**)*

The title compound **8-Fe–Pd** was synthesized by using the same synthesis methodology as **5-Fe–Pd**, whereby 275 mg (0.13 mmol) of $[CH_2N(CH_2CH_2C(O)NHCH_2CH_2NHC(O)(Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_4PPh_2)))_2]_2$ (**8-Fe**) were reacted with 100 mg (0.27 mmol) of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (**4**). After appropriate work-up, **8-Fe–Pd** was obtained as a bright yellow solid (240 mg, 65 %, based on **8-Fe**). Mp: 170 °C. Anal. Calc for $C_{126}H_{136}Cl_4Fe_4N_{10}O_8P_4Pd_4$ (2833.3): C, 53.41; H, 4.84; N, 4.94. Found: C, 53.74; H, 4.96; N, 5.28. $^1$H NMR ($\delta$, $CDCl_3$): 2.34 (m, 8 H, $CH_2C(O)$), 2.42 (m, 4 H, $CH_2N$), 2.74 (m, 8 H, $NCH_2CH_2C(O)$), 2.84 (m, 4 H, C*H*-*anti*), 3.38 (m, 16 H, $HNCH_2CH_2NH$), 3.81 (m, 4 H, C*H*-*syn*), 4.07 (m, 8 H, $H_\alpha/C_5H_4PPh_2$), 4.28 (m, 8 H, $H_\beta/C_5H_4C(O)$), 4.55 (m, 8 H, $H_\beta/C_5H_4PPh_2$), 5.01 (m, 8 H, $H_\alpha/C_5H_4C(O)$), 5.61 (m, 4 H, C*H*-*centered*), 7.28–7.78 (m, 40 H, $C_6H_5$), 8.18 (m, 8 H, N*H*). $^{13}$C{$^1$H} NMR ($\delta$, $CDCl_3$): 34.8 ($CH_2C(O)$), 39.3 ($HNCH_2CH_2NH$), 40.4 ($HNCH_2CH_2NH$), 53.5 ($NCH_2CH_2C(O)$), 56.7 ($CH_2N$), 61.2 ($CH_2$-*syn*/*anti*), 70.4 ($C_\alpha/C_5H_4C(O)$), 72.4 ($C_\beta/C_5H_4C(O)$), 73.8 (d, $^3J_{CP}$ = 7 Hz, $C_\beta/C_5H_4C(PPh_2)$), 74.5 (d, $^1J_{CP}$ = 48 Hz, $C_i/C_5H_4C(PPh_2)$), 76.2 ($C_\alpha/C_5H_4C(PPh_2)$), 77.9 ($C_i/C_5H_4C(O)$), 118.3 (C*H*-*centered*), 128.5 (d, $^3J_{CP}$ = 10 Hz, $C_m/C_6H_5$), 130.4 ($C_p/C_6H_5$), 133.1 (d, $^2J_{CP}$ = 12 Hz, $C_o/C_6H_5$), 133.6 (d, $^1J_{CP}$ = 48 Hz, $C_i/C_6H_5$), 169.9 (*C*(O)), 170.4 (*C*(O)). $^{31}$P{$^1$H} NMR ($\delta$, $CDCl_3$): 13.4 (*P*Ph$_2$). IR (KBr, cm$^{-1}$): 3300 (m, $\nu_{NH}$), 1645 (s, $\nu_{C(O)}$, amide I), 1535 (s, $\nu_{C(O)}$, amide II), 1480 (w, $\nu_{\eta^3\text{-}C_3H_5}$).

### *4.8. Preparation of $(Fe((\eta^5\text{-}C_5H_4PPh_2(Pd(\eta^3\text{-}C_3H_5)Cl))(\eta^5\text{-}C_5H_4))C(O)HNCH_2CH_2NHC(O)CH_2CH_2)N[CH_2CH_2N(CH_2CH_2C(O)NHCH_2CH_2NHC(O)(Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_4PPh_2(Pd(\eta^3\text{-}C_3H_5)Cl))))_2]_2$ (**9-Fe–Pd**)*

Dendrimer **9-Fe–Pd** was synthesized in the same manner as **5-Fe–Pd**, whereby 150 mg (0.06 mmol) of $(Fe((\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_4))C(O)HNCH_2CH_2NHC(O)CH_2CH_2)N[CH_2CH_2N(CH_2CH_2C(O)NHCH_2CH_2NHC(O)(Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_4PPh_2)))_2]_2$ (**9-Fe**) were reacted with 55 mg (0.15 mmol) of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (**4**). After appropriate work-up, **9-Fe–Pd** was obtained as a bright yellow solid (180 mg, 85 %, based on **9-Fe**). Mp: 170 °C. Anal. Calc for $C_{159}H_{173}Cl_5Fe_5N_{13}O_{10}P_5Pd_5$ (3569.6): C, 53.50; H, 4.88; N, 5.10. Found: C, 54.02; H, 4.75; N, 5.43. $^1$H NMR ($\delta$, $CDCl_3$): 2.31 (m, 20 H, $NCH_2CH_2C(O)$), 2.58 (m, 8 H, $NCH_2CH_2N$), 2.76 (m, 5 H, C*H*-*anti*), 3.31 (m, 20 H, $HNCH_2CH_2NH$), 3.79 (m, 5 H, C*H*-*syn*), 4.04 (m, 10 H, $H_\alpha/C_5H_4PPh_2$), 4.28 (m, 10 H, $H_\beta/C_5H_4C(O)$), 4.53 (m, 10 H, $H_\beta/C_5H_4PPh_2$), 5.01 (m, 10 H, $H_\alpha/C_5H_4C(O)$), 5.62 (m, 5 H, C*H*-*centered*), 7.27–7.76 (m, 50 H, $C_6H_5$), 7.89 (m, 10 H, N*H*). $^{13}$C{$^1$H} NMR ($\delta$, $CDCl_3$): 34.6 ($CH_2C(O)$), 39.5 ($HNCH_2CH_2NH$), 40.1 ($HNCH_2CH_2NH$), 50.9 ($NCH_2CH_2C(O)$), 53.5 ($CH_2N$), 61.3 ($CH_2$-*syn*/*anti*), 70.3 ($C_\alpha/C_5H_4C(O)$), 72.5 ($C_\beta/C_5H_4C(O)$), 73.9 (d, $^3J_{CP}$ = 7 Hz, $C_\beta/C_5H_4C(PPh_2)$), 74.5 (d, $^1J_{CP}$ = 46 Hz, $C_i/C_5H_4C(PPh_2)$), 77.2 ($C_\alpha/C_5H_4C(PPh_2)$), 77.8 ($C_i/C_5H_4C(O)$), 118.4 (C*H*-*centered*), 128.5 (d, $^3J_{CP}$ = 11 Hz, $C_m/C_6H_5$), 130.4 ($C_p/C_6H_5$), 133.2 (d, $^2J_{CP}$ = 11 Hz, $C_o/C_6H_5$), 133.4 (d, $^1J_{CP}$ = 44 Hz, $C_i/C_6H_5$), 170.0 (*C*(O)), 170.8 (*C*(O)). $^{31}$P{$^1$H} NMR ($\delta$, $CDCl_3$): 13.3 (*P*Ph$_2$). IR (KBr, cm$^{-1}$): 3295 (m, $\nu_{NH}$), 1640 (s, $\nu_{C(O)}$, amide I), 1540 (s, $\nu_{C(O)}$, amide II), 1480 (w, $\nu_{\eta^3\text{-}C_3H_5}$).

### 4.9. *Preparation of* $(Fe(\eta^5\text{-}C_5H_4(PPh_2(Se))(\eta^5\text{-}C_5H_4C(O)NH^nC_3H_7)))$ (***5-Fe–Se***)

Fifty milligrams (0.11 mmol) of $(Fe(\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_4C(O)NH^nC_3H_7))$ (**5-Fe**) were dissolved in 10 mL of dichloromethane and 8 mg (0.11 mmol) of selenium were added in a single portion. After 1 h of stirring at 25 °C, the suspension was filtered through a pad of Celite. After evaporation the title compound could be isolated as an orange solid (55 mg, 98 %, based on **5-Fe**). Anal. Calc for $C_{26}H_{26}FeNOPSe$ (534.3): C, 58.45; H, 4.91; N, 2.62. Found: C, 58.16; H, 5.22; N, 2.54. $^1H$ NMR ($\delta$, $CDCl_3$): 0.97 (t, 3 H, $^3J_{HH} = 7.3$ Hz, $CH_3$), 1.67 (m, 2 H, $CH_2CH_2CH_3$), 3.33 (m, 2 H, $CH_2CH_2CH_3$), 3.92 (m, 2 H, $H_\alpha/C_5H_4PPh_2$), 4.24 (m, 2 H, $H_\beta/C_5H_4C(O)$), 4.62 (m, 2 H, $H_\beta/C_5H_4PPh_2$), 4.89 (m, 2 H, $H_\alpha/C_5H_4C(O)$), 7.39 (m, 1 H, NH), 7.45–7.68 (m, 10 H, $C_6H_5$). $^{13}C\{^1H\}$ NMR ($\delta$, $CDCl_3$): 11.8 ($CH_3$), 23.2 ($CH_2CH_2CH_3$), 41.4 ($CH_2CH_2CH_3$), 71.2 ($C_\alpha/C_5H_4C(O)$), 71.5 ($C_\beta/C_5H_4C(O)$), 73.4 (d, $^3J_{CP} = 10$ Hz, $C_\beta/C_5H_4C(PPh_2)$), 75.1 (d, $^2J_{CP} = 12$ Hz, $C_\alpha/C_5H_4C(PPh_2)$), 75.5 (d, $^1J_{CP} = 88$ Hz, $C_i/C_5H_4C(PPh_2)$), 79.1 ($C_i/C_5H_4C(O)$), 128.4 (d, $^3J_{CP} = 12$ Hz, $C_m/C_6H_5$), 131.7 ($C_p/C_6H_5$), 132.1 (d, $^1J_{CP} = 11$ Hz, $C_i/C_6H_5$), 133.2 (d, $C_o/C_6H_5$), 169.1 ($C(O)$). $^{31}P\{^1H\}$ NMR ($\delta$, $CDCl_3$): 30.9 $^1J_{(^{31}P-^{77}Se)} = 720$ Hz). IR (KBr, $cm^{-1}$): 3300 (m, $\nu_{NH}$), 1645 (s, $\nu_{C(O)}$, amide I), 1540 (s, $\nu_{C(O)}$, amide II), 560 (s, $\nu_{P(Se)}$).

### 4.10. *Preparation of* $(Fe((\eta^5\text{-}C_5H_4PPh_2(Se))(\eta^5\text{-}C_5H_4))C(O)HNCH_2CH_2NHC(O)CH_2CH_2)N[CH_2CH_2N(CH_2CH_2C(O)NHCH_2CH_2NHC(O)(Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_4(PPh_2(Se)))))_2]_2$ (***9-Fe–Se***)

Compound **9-Fe–Se** was synthesized as described for **5-Fe–Se** using 55 mg (0.02 mmol) of $(Fe((\eta^5\text{-}C_5H_4PPh_2)(\eta^5\text{-}C_5H_4))C(O)HNCH_2CH_2NHC(O)CH_2CH_2)N[CH_2CH_2N(CH_2CH_2C(O)NHCH_2CH_2NH\text{-}C(O)(Fe(\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_4PPh_2)))_2]_2$ (**9-Fe**) and 8 mg (0.11 mmol) of selenium. After appropriate work-up, compound **9-Fe–Se** was obtained as an air stable, orange colored solid (50 mg, 85 %, based on **9-Fe**). Anal. Calc for $C_{144}H_{148}Fe_5N_{13}O_{10}P_5Se_5$ (3049.7): C, 56.71; H, 4.89; N, 5.97. Found: C, 56.31; H, 4.94; N, 6.02. $^1H$ NMR ($\delta$, $CDCl_3$): 2.03 (m, 20 H, $NCH_2CH_2C(O)$), 2.67 (m, 8 H, $NCH_2CH_2N$), 3.47 (m, 20 H, $HNCH_2CH_2NH$), 4.15 (m, 10 H, $H_\alpha/C_5H_4PPh_2$), 4.32 (m, 10 H, $H_\beta/C_5H_4C(O)$), 4.59 (m, 10 H, $H_\beta/C_5H_4PPh_2$), 4.88 (m, 10 H, $H_\alpha/C_5H_4C(O)$), 7.45–7.67 (m, 50 H, $C_6H_5$), 7.72 (m, 10 H, NH). $^{13}C\{^1H\}$ NMR ($\delta$, $CDCl_3$): 29.8 ($CH_2C(O)$), 39.7 ($HNCH_2CH_2NH$), 40.5 ($HNCH_2CH_2NH$), 50.3 ($NCH_2CH_2C(O)$), 51.6 ($NCH_2CH_2N$), 51.9 ($NCH_2CH_2N$), 70.1 ($C_\alpha/C_5H_4C(O)$), 72.1 ($C_\beta/C_5H_4C(O)$), 73.7 (d, $^3J_{CP} = 8$ Hz, $C_\beta/C_5H_4C(PPh_2)$), 75.4 (d, $^2J_{CP} = 11$ Hz, $C_\alpha/C_5H_4C(PPh_2)$), 75.6 (d, $^1J_{CP} = 88$ Hz, $C_i/C_5H_4C(PPh_2)$), 78.2 ($C_i/C_5H_4C(O)$), 128.3 (d, $^3J_{CP} = 12$ Hz, $C_m/C_6H_5$), 131.5 ($C_p/C_6H_5$), 132.2 (d, $^1J_{CP} = 11$ Hz, $C_i/C_6H_5$), 133.2 ($C_o/C_6H_5$), 170.1 ($C(O)$), 173.2 ($C(O)$). $^{31}P\{^1H\}$ NMR ($\delta$, $CDCl_3$): 30.7 ($^1J_{(^{31}P-^{77}Se)} = 723$ Hz). IR (KBr, $cm^{-1}$): 3300 (m, $\nu_{NH}$), 1645 (s, $\nu_{C(O)}$, amide I), 1540 (s, $\nu_{C(O)}$, amide II), 560 (s, $\nu_{P(Se)}$).

### 4.11. *General Procedure for the Heck reaction*

Iodobenzene (615 mg, 3.0 mmol), *tert*-butyl acrylate (395 mg, 3.1 mmol), $EtN^iPr_2$ (410 mg, 3.1 mmol), and acetylferrocene (114 mg, 0.5 mmol) were dissolved in 20 mL of a toluene/acetonitrile mixture (ratio 1:1, v/v) and loaded with the respective catalyst (**6-Fe–Pd** to **9-Fe–Pd** or **5-Fe–Pd**, 0.5 mol% palladium). Two equivalents of [CuI] (6 mg, 0.0315 mmol) were added in a single portion. The reaction suspension was stirred at 80 °C and samples (1 mL) were taken in periods of 1 h. The samples were filtered through a pad of Silica gel with diethyl ether as eluent. All volatiles were evaporated from the respective samples under reduced pressure. The conversions were determined by $^1H$ NMR spectroscopy.

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