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trans-Spanning ferrocene amidodiphosphine ligand: Synthesis, palladium complexes and catalytic use in Suzuki–Miyaura cross-coupling

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ABSTRACT

Amide coupling between [2-(diphenylphosphino)phenyl]methylamine and 1′-(diphenylphosphino)ferrocene-1-carboxylic acid (Hdpf) afforded a novel diphosphine-amide, 1-{*N*-[(2-(diphenylphosphino)phenyl)methyl]carbamoyl}-1′-(diphenylphosphino)ferrocene (**1**), which was subsequently studied as a ligand for palladium(II) complexes. Depending on the metal precursor, the following complexes were isolated: [$PdCl_2$(**1**-κ^2*P*,*P*′)] (**2**), [PdCl(Me)(**1**-κ^2*P*,*P*′)] (**3**), [(μ-**1**){$PdCl_2(PBu_3)$}$_2$] (**4**) and [(μ-**1**){PdCl(L^{NC})}$_2$] (L^{NC} = 2-[(dimethylamino-κ*N*)methyl]phenyl-κC^1), featuring this ligand either as a *trans*-chelating or as a P,P′-bridging donor. The crystal structure of **2**·1.25CH_2Cl_2 was established by X-ray crystallography, corroborating that **1** coordinates as a *trans*-spanning diphosphine without any significant distortion to the coordination sphere. Complex **2** together with a catalyst prepared *in situ* from **1** and palladium(II) acetate were tested in Suzuki–Miyaura reaction of aryl bromides with phenylboronic acid in dioxane.

1. Introduction

Bidentate ligands capable of traversing *trans* coordination sites have originally attracted attention as chemical curiosities. Later on, however, they proved practically useful for the elucidation of ligand steric effects in coordination compounds, for fundamental studies on metal-mediated reactions and in catalysis. The most frequently encountered *trans*-spanning ligands are undoubtedly diphosphines, whose donor moieties are pre-arranged with an aid of an organic backbone into positions appropriate for the formation of *trans*-chelates [1]. Less attention has been paid to other symmetric ligands (e.g., to N,N-type [2] and bis-carbene ligands [3]) and, particularly, to their donor-unsymmetric counterparts (e.g., to P,N-donors [4]).

While extending our studies on ferrocene phosphinocarboxylic acids [5,6], we recently turned also to their carboxamide derivatives. So far, we have demonstrated that even simple phosphinoferrocene carboxamides are versatile ligands for coordination chemistry and catalysis [6b,6g,7], and valuable organometallic synthetic building blocks [8]. Ferrocene phosphinocarboxylic amides are usually readily accessible by reaction of the appropriate amines with phosphinocarboxylic acids in the presence of peptide coupling agents or, alternatively, via active phosphinocarboxylic pentafluorophenyl esters [7–9]. As these methods are relatively mild and tolerate numerous functional groups, they can be advantageously utilised in the preparation of N-functionalised amides. Such donors are highly structurally versatile and potentially multidentate, thus markedly widening the spectrum of accessible ferrocene phosphinocarboxamides as well as their application field, particularly towards coordination chemistry and catalysis. Validity of this approach has been already demonstrated by the synthesis of ferrocene phosphinocarboxamides from pyridyl-substituted [7a,d] and 2-hydroxyethyl amines [10], and from amino acid esters [11].

During our studies on the former ligands, we found that N-(pyrid-2-yl)methyl amide **I** (see Chart 1) reacts with [$PdCl_2$(cod)] (cod = η^2:η^2-cycloocta-1,5-diene) to give *trans*-chelate or bisphosphine palladium(II) complexes depending on the metal-to-ligand ratio [7a]. This property led us to design an analogue to amide **I**, in which the pyridine nitrogen is replaced with a "C-PPh_2" moiety (compound **1**). Herein, we report the preparation of this novel diphosphine-amide and several palladium complexes thereof. We also describe the crystal structure of [$PdCl_2$(**1**-κ^2*P*,*P*′)] featuring this diphosphine as a *trans*-chelating donor and preliminary results of catalytic testing of this complex in Suzuki–Miyaura cross-coupling.

2. Results and discussion

2.1. Synthesis and spectroscopic characterisation of the ligand

Diphosphine-amide **1** was synthesised by amide coupling of [2-(diphenylphosphino)phenyl]methylamine to 1′-(diphenylphosphino)ferrocene-1-carboxylic acid (Hdpf) in the presence of 1-hydroxybenzotriazole (HOBt) and *N*-[3-(dimethylamino)

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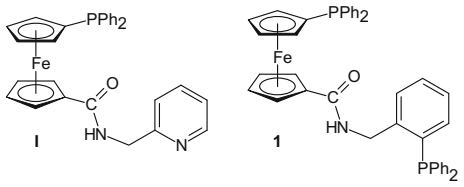
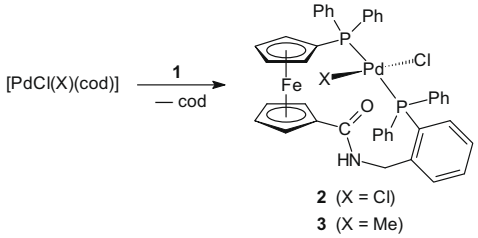


Chart 1.



Scheme 2.

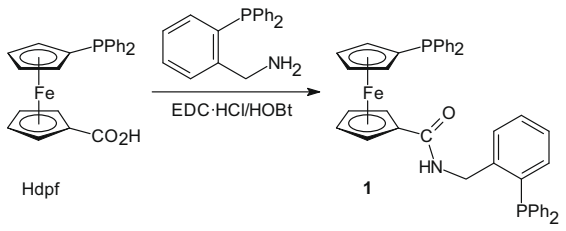
propyl]-*N*′-ethylcarbodiimide hydrochloride (EDC·HCl; Scheme 1). Isolation by column chromatography followed by crystallisation from ethyl acetate-hexane afforded **1** as an air-stable, orange solid in a 67% yield.

Compound **1** was characterised by conventional spectroscopic methods (NMR, IR and MS) and by combustion analysis. In IR spectra, it showed characteristic strong amide bands at 1632 and 1553 cm^{-1}. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **1** were consistent with the formulation, combining the signals due to the 1,1′-disubstituted ferrocene unit, the amide pendant ($CONHC_6H_4$) and two chemically different PPh_2 groups at the expected positions. The amide proton was observed as a methylene-coupled triplet at δ_H 5.94 whereas its bonded methylene resonated at δ_H 4.69, being observed as a double doublet due to coupling with the amide proton and the proximal phosphorus atom ($^{3}J_{HH}$ = 6.1, $^{4}J_{PH}$ = 1.1 Hz). In $^{13}C\{^{1}H\}$ NMR spectrum, the methylene group was observed as a phosphorus-coupled doublet at δ_C 42.2 ($^{3}J_{PC}$ = 21 Hz) while the carbonyl group signal was found at δ_C 169.34 (*cf.* δ_C 177.2 for Hdpf [12]). Finally, the $^{31}P\{^{1}H\}$ NMR spectrum comprised two sharp singlets at δ_P −14.7 and −17.0 attributable to benzene- and ferrocene-bound PPh_2 groups, respectively. The position of the latter signal corresponds with that of the parent acid (Hdpf: δ_P −17.6 [12]) and its amides [7,8].

2.2. Preparation of palladium(II) complexes

The reaction between equimolar amounts of **1** and $[PdCl_2(cod)]$ gave complex $[PdCl_2(\mathbf{1})]$ (**2**) featuring the bis-phosphine as a *trans*-chelating ligand (Scheme 2). A similar reaction with [PdCl(Me)(cod)] afforded an analogous complex [PdCl(Me)(**1**)] (**3**) (Scheme 2). Surprisingly, complexes **2** and **3** resulted also when **1** was reacted with the respective dimers $[\{Pd(\mu\text{-}Cl)(X)(PMe_3)\}_2]$ (X = Cl, Me). Formation of the chelated monopalladium complexes from the chloride-bridged dinuclear precursors is most likely a stepwise process, consisting of primary bridge-cleavage reaction and a subsequent intramolecular, chelate-assisted substitution of the PMe_3 ligand [13].

Complexes **2** and **3** tend to retain solvents in their structures, crystallising as dichloromethane adducts. Their formulation was established from IR, electrospray (ESI) MS and NMR spectra, and confirmed by elemental analyses. Besides, the solid-state structure of **2** was established by X-ray diffraction analysis (*vide infra*). Spectral data of **2** and **3** clearly indicate that ligand **1** coordinates as a chelating diphosphine. The amide bands in IR spectra are observed



Scheme 1.

at positions similar to those of free **1**, thereby ruling out the involvement of the amide moiety in coordination. On the other hand, the $^{31}P\{^{1}H\}$ NMR spectra display pairs of doublets due to the interacting non-equivalent phosphorus atoms ($^{2}J_{PP}$ = 572 Hz for **2**, 437 Hz for **3**), that are shifted to lower fields compared with the free ligand. Whereas the ^{1}H NMR spectrum of **2** displays four resonances attributable to the ferrocene CH groups (AA′BB′ and AA′BB′X spin systems; A, B = ^{1}H, X = ^{31}P), the ferrocene protons in the spectrum of complex **3** are observed non-degenerate (eight resonances) because of a lowered molecular symmetry.

It is also noteworthy that ^{1}H NMR spectrum of **2** recorded at room temperature displays some signals markedly broadened. A variable temperature (VT) NMR study (Fig. 1) confirmed such signal broadening to reflect a molecular dynamics slow at the NMR time scale. Whereas warming to 50 °C caused a sharpening of the proton resonances (except for one ferrocene CH signal at δ_H ca. 4.54 which remained broad even at this temperature), cooling to 0 °C and further down to −25 °C resulted in broadening of the resonances, particularly those attributable to the ferrocene unit. The observed dynamic behaviour apparently results from a limited conformational mobility of the ligand molecule imparted by its *trans*-chelate coordination.

In contrast to its PMe_3-analogue, complex $[\{Pd(\mu\text{-}Cl)Cl(PBu_3)\}_2]$ reacted with **1** to give the expected bridge-cleavage product **4** (Scheme 3). Such difference in reactivity can be attributed to unlike steric and electronic properties of the two phosphines. Tributylphosphine is not only a stronger donor than PMe_3 but also provides a better steric protection to the metal centre, which both make any intramolecular ligand substitution more difficult. Another dipalladium complex involving diphosphine **1** as a P,P′-bridging ligand, compound **5**, was obtained by bridge-splitting reaction from the dimer $[\{Pd(\mu\text{-}Cl)(L^{NC})\}_2]$, where L^{NC} = 2-[(dimethylamino-κ*N*)methyl]phenyl-κC^1 (Scheme 3). Similarly to their monopalladium counterparts, complexes **4** and **5** show the ^{31}P NMR signals shifted to lower fields compared to free **1** though as singlets owing to an absence of a scalar P–P coupling. The IR spectra of **4** and **5** suggested the presence of uncoordinated amide moieties.

2.3. The crystal structure of complex *2*

The solid-state structure of complex **2** has been determined for its solvate **2**·1.25$CHCl_3$. Views of the complex molecule are shown in Fig. 2. Selected geometric data are listed in Table 1. At first sight, the structure determination corroborates the expected *trans*-chelate coordination of the diphosphine ligand. The Pd-donor bond lengths correspond well with the distances reported for *trans*-$[PdCl_2L_2]$ complexes, where L is P-monodentate Hdpf [14] or $Ph_2PfcCONHCH_2(C_5H_4N\text{-}2)$ (fc = ferrocene-1,1′-diyl) [7a]. As indicated by the interligand angles, the diphosphine spans the *trans* positions with only a minor distortion of the coordination plane around palladium. The ligand bite angle P1-Pd-P(2) is 171.91(3)°, not far from the ideal 180°. A minor deviation from the regular geometry can be demonstrated also by the difference in the Cl(*n*)-Pd-P(1,2) angles (4.3° for *n* = 1; 5.4° for *n* = 2) or, alternatively

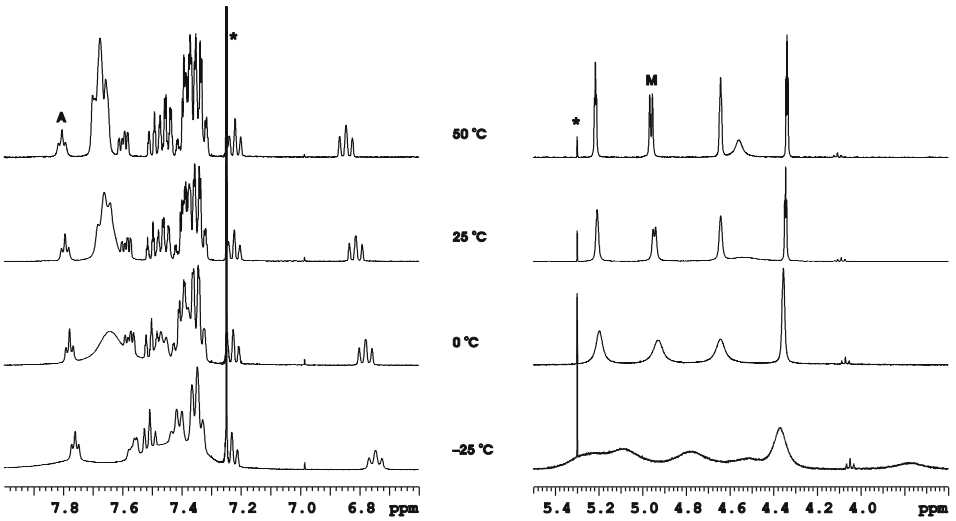
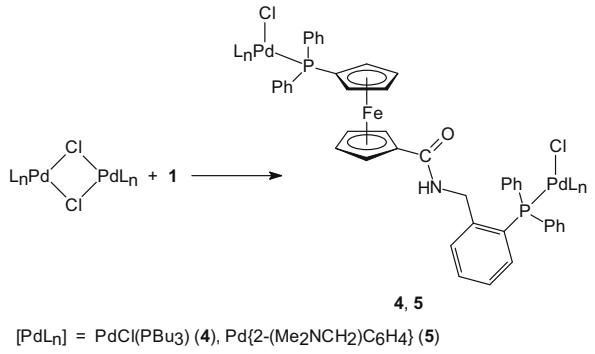


Fig. 1. VT ^{1}H NMR spectra of complex **2** in the region of the aromatic and NH (left) and cyclopentadienyl and CH_2 protons (right). **A** and **M** denote the signals due to amide NH and NH-bonded methylene protons, respectively. The asterisks indicate residual solvent signals (CH_2Cl_2 and $CHCl_3$).



Scheme 3.

by the angle subtended by the Cl(1)···Cl(2) and P(1)···P(2) vectors being 87.55(2)°. When viewed along the P(1)···P(2) line (Fig. 2b), the chloride ligands are observed somewhat displaced towards the amide moiety whilst the phosphorus atoms decline in the opposite direction, all deviating from the common least-squares $\{PdCl_2P_2\}$ plane by ca. 0.16 Å. Yet, the sum of the interligand angles (361.1°) rules out any pronounced tetrahedral deformation.

The $\{PdCl_2P_2\}$ plane and the Cp(1) ring are mutually rotated by 57.2(1)° which, together with the bending of the chloride atoms, aids the formation of intramolecular hydrogen bonds N–H(1N)···Cl(2) [N···Cl(2) = 3.439(3) Å, N–H(1N)···Cl(2) = 157°]. Notably, the chelating ligand is flexible enough to allow for a staggered conformation of the 'PC_3' units, which likely represents the least sterically congested orientation of the two bulky phosphine moieties (Fig. 2b). The ferrocene moiety displays nearly identical Fe-ring centroid distances and a tilt of 4.6(2)°. Conformation of the 1,1′-disubstituted ferrocene unit is close to *syn*-eclipsed with the torsion angle C(1)–Cg(1)–Cg(2)–C(6) being 68° (*cf.* the ideal value of 72°). Despite the intramolecular hydrogen bonding interaction, the amide {C(11)ON} moiety and the Cp(2) ring are nearly coplanar (dihedral angle 5.1(4)°). On the other hand, the C(25–30) benzene ring is practically perpendicular to both the coordination plane

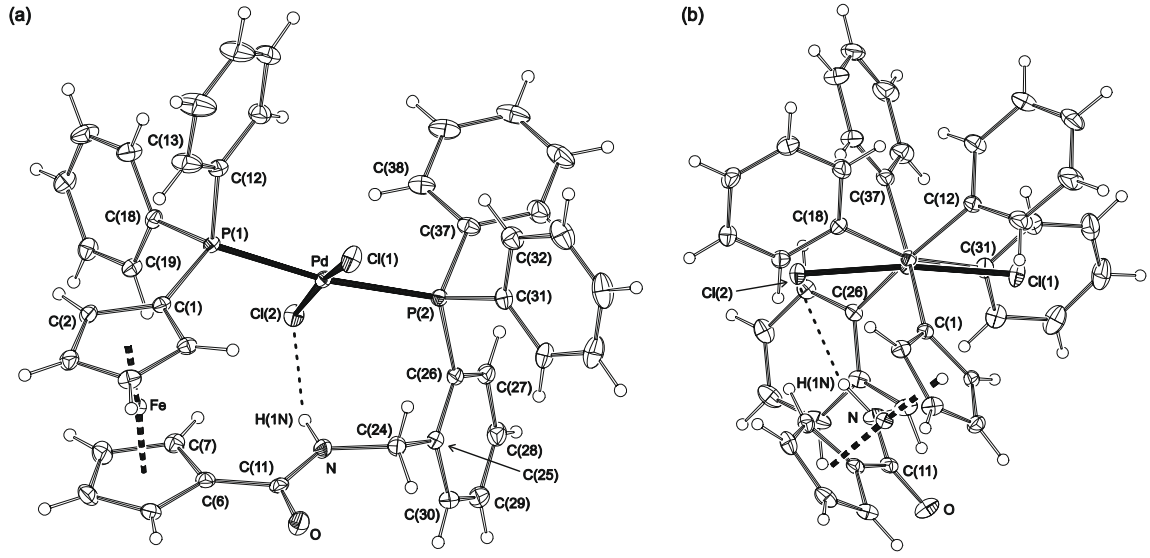


Fig. 2. PLATON plots of the complex molecule in the crystal structure of **2**·1.25$CHCl_3$: (a) a general view, and (b) a view in the P(1)···P(2) direction. Displacement ellipsoids enclose the 30% probability level. The intramolecular hydrogen bond N–H(1N)···Cl(2) is indicated with a dashed line.

Table 1
Selected distances and angles for **2**·1.25 $CHCl_3$ (in Å and °).[a]

Distances		Angles	
Pd–Cl(1)	2.2932(8)	Cl(1)–Pd–P(1)	87.61(3)
Pd–Cl(2)	2.3074(8)	Cl(1)–Pd–P(2)	91.95(3)
Pd–P(1)	2.3321(7)	Cl(2)–Pd–P(1)	93.50(3)
Pd–P(2)	2.3496(9)	Cl(2)–Pd–P(2)	88.07(3)
Fe–Cg(1)	1.656(1)	∠Cp(1), Cp(2)	4.6(2)
Fe–Cg(2)	1.663(2)	O–C(11)–N	123.0(3)
C(11)–O	1.235(4)	C(11)–N–C(24)	122.5(3)
C(11)–N	1.344(4)	N–C(24)–C(25)	109.9(2)
N–C(24)	1.467(4)	C(24)–C(25)–C(26)	122.7(3)
P(1)–C(1)	1.800(3)	O–C(11)–N–C(24)	4.8(5)
P(1)–C(12)	1.815(3)	C(24)–C(25)–C(26)–P(2)	175.0(3)
P(1)–C(18)	1.826(3)	Pd–P(1)–C[b]	107.4(1)–119.3(1)
P(2)–C(26)	1.820(3)	C–P(1)–C[c]	103.7(1)–105.3(1)
P(2)–C(31)	1.827(3)	Pd–P(2)–C[d]	109.0(1)–118.7(1)
P(2)–C(37)	1.829(3)	C–P(2)–C[e]	101.71(1)–106.5(1)

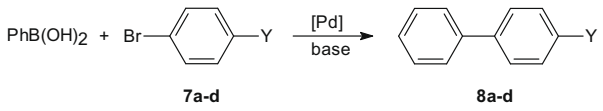
[a] Definition of the ring planes: Cp(1) = C(1–5), Cp(2) = C(6–10). Cg(1) and Cg(2) denote the respective centroids.
[b] The range of Pd–P(1)–C(1,12,18) angles.
[c] The range of C(1)–P(1)–C(12,18) and C(12)–P(1)–C(18) angles.
[d] The range of Pd–P(2)–C(26,31,37) angles.
[e] The range of C(26)–P(2)–C(31,37) and C(31)–P(2)–C(37) angles.

(dihedral angle 86.8(1)°) and the Cp(2) ring (dihedral angle 84.0(2)°).

2.4. Catalytic experiments

Both the defined complex **2** and a catalyst generated *in situ* by mixing ligand **1** with the equimolar amount of palladium(II) acetate have been tested in Suzuki–Miyaura cross-coupling [15] of phenylboronic acid to give 4-substituted aryl bromides (Scheme 4). The reactions were performed with 0.5 mol.% palladium pre-catalyst using dioxane as the solvent at 90 °C for 18 h.

The data collected in Table 2 demonstrate that both catalysts efficiently promote the coupling reaction, the *in situ* generated pre-catalyst giving only slightly lower conversions. The reactions performed with activated aryl halides (**7a,b**) proceed quantitatively whereas those involving derivatives bearing electron-donating groups (OMe and Me) gave somewhat lower but still very good conversions. Although the current results may not be astonishing in view of the recently developed, highly active cross-coupling catalysts [15], they clearly indicate that the *trans*-coordination preference of the diphosphine ligand does not compromise the coupling reaction (i.e., it does not prevent the formation of catalytically active, presumably Pd(0) species) [1a,16]. In view of the previous studies on Suzuki–Miyaura reactions catalysed with Pd-complexes with organic *trans*-chelating diphosphines, the catalytic activity of **1**-based systems could be explained by *trans*-to-*cis* isomerisation during catalyst activation, by partial dissociation of the bidentate ligand (open-arm mechanism) or by formation of some dinuclear intermediates [17]. Alternative rationalisation can be sought in the formation of fine metal particles (particularly at elevated temperatures) that were shown to efficiently promote the cross-coupling reactions [18]. The latter explanation seems to be supported by mercury poisoning tests [19]. Addition of mercury to the reaction system *after* stirring for 5 min at the reaction temperature caused the coupling reaction to stop. After 18 h, the *in situ* catalyst (**1**/$Pd(OAc)_2$) gave the coupling product **8d** with ca. 5% conversion while no coupling product was detected when complex **2** was used as the catalyst. Control experiments performed in parallel without added mercury proceeded normally.



Scheme 4. Suzuki–Miyaura cross-coupling of aryl bromides **7a–e** to give substituted biphenyl **8a–e** (Y = NO_2 (**a**), Ac (**b**), OMe (**c**), and Me (**d**)).

Table 2
Application of **1** to Suzuki–Miyaura cross-coupling of aryl bromides.[a]

Substrate (Y)	Conversion to biphenyl **8**	
	2	$Pd(OAc)_2$-**1**[b]
Y = NO_2 (**7a**)	Quant.	Quant.
Y = C(O)Me (**7b**)	Quant.	Quant.
Y = OMe (**7c**)	83	78
Y = Me (**7d**)	93	85

[a] The reactions were performed with 0.5 mol.% of the catalyst and 1.5 equiv. of $PhB(OH)_2$ at 90 °C for 18 h. Conversions were determined from integration of ^{1}H NMR spectra and are an average of two independent runs. For further details, see Section 4.
[b] Catalyst generated *in situ*.

3. Conclusions

Amidophosphine **1** is readily accessible from amide coupling of 1′-(diphenylphosphino)ferrocene-1-carboxylic acid (Hdpf) with [2-(diphenylphosphino)phenyl]methylamine. The particular disposition of the donor atoms and limited mobility of the molecular scaffold enable this unsymmetric P,P-donor to form *trans*-chelate or bridged dinuclear complexes with palladium(II) in dependance on the metal source. The formation of *trans*-chelates was shown to proceed either directly or via ligand-displacement route. As evidenced by the structural data for **2** the diphosphine-amide coordinates to palladium without any significant deformation of the coordination environment around the central atom. Both the defined complex **2** and the **1**-$Pd(OAc)_2$ system catalyse Suzuki–Miyaura cross-coupling of aryl bromides and phenylboronic acid to give the corresponding biphenyls.

4. Experimental

4.1. Materials and methods

The syntheses were performed under argon atmosphere with an exclusion of the direct daylight. Dichloromethane was pre-dried by standing over anhydrous potassium carbonate and then distilled from calcium hydride under argon. Dioxane was dried with sodium metal and distilled under argon. [2-(Diphenylphosphino) phenyl]methylamine [20] was prepared by reduction of 2-(diphenylphosphino)benzonitrile [21]. Hdpf [12], $[PdCl_2(cod)]$ (cod = η^2:η^2-cycloocta-1,5-diene) [22], [PdCl(Me)(cod)] [23], $[\{Pd(\mu\text{-}Cl)(Me)(PMe_3)\}_2]$ [13], $[\{Pd(\mu\text{-}Cl)Cl(PR_3)\}_2]$ (R = Me and Bu) [24], and $[\{Pd(\mu\text{-}Cl)(L^{NC})\}_2]$ [25] were prepared by the literature procedures. Other chemicals (Lachema, Fluka) and solvents used for crystallisations and chromatography (Penta) were used without purification.

NMR spectra were measured with a Varian Unity Inova spectrometer (^{1}H, 399.95; ^{13}C, 100.58; ^{31}P, 161.90 MHz) at 25 °C unless indicated otherwise. Chemical shifts (δ) are given relative to internal tetramethylsilane (^{13}C and ^{1}H) or to external 85% aqueous H_3PO_4 (^{31}P), all set to 0 ppm. Signals of residual solvents (if applicable) are omitted from the signal list. IR spectra were recorded with an FT IR Nicolet Magna 650 spectrometer. Positive-ion electrospray (ESI+) mass spectra were recorded on a Bruker Esquire 3000 instrument. The samples were dissolved in chloroform or dichloromethane and the solution was diluted with methanol in large excess. Fast atom bombardment (FAB) mass spectra were

recorded on a ZAB EQ spectrometer in 3-nitrobenzylalcohol matrix. The melting points were determined on a Kofler block and are uncorrected.

4.2. Preparation of 1-{N-[(2-(diphenylphosphino)-phenyl)methyl]carbamoyl}-1′-(diphenylphosphino)ferrocene (**1**)

1-Hydroxybenzotriazole (297 mg, 2.2 mmol) was added to a solution of Hdpf (828 mg, 2.0 mmol) in dry dichloromethane (10 mL). The mixture was cooled in an ice bath and treated with *N*-{3-(dimethylamino)propyl}-*N*′-ethylcarbodiimide hydrochloride (EDC·HCl; 422 mg, 2.2 mmol), whereupon the solid triazole quickly dissolved to give an orange red solution. After stirring for 30 min at 0 °C, a solution of [2-(diphenylphosphino)phenyl]methylamine (640 mg, 2.2 mmol) in dichloromethane (5 mL) was introduced and the reaction solution was stirred at room temperature overnight. Then, it was washed successively with 3 M HCl, saturated aqueous $NaHCO_3$ and brine (50 mL each), dried over $MgSO_4$, and evaporated under reduced pressure. The yellow orange residue was purified by column chromatography (silica gel, methanol–dichloromethane 1:20, *v*/*v*). The first orange band due to the amide was collected and evaporated under vacuum to give an orange solid. Subsequent recrystallisation from ethyl acetate–hexane afforded analytically pure **1** as a yellow orange microcrystalline solid. Yield: 0.923 g (67%).

M.p. 102–103 °C (ethyl acetate–hexane). ^{1}H NMR ($CDCl_3$): δ 4.05 (apparent q, $J \approx 2$ Hz, 2 H, fc), 4.14 (apparent t, $J \approx 2$ Hz, 2H, fc), 4.28 (apparent t, $J \approx 2$ Hz, 2H, fc), 4.33 (apparent t, $J \approx 2$ Hz, 2H, fc), 4.69 (dd, $^3J_{HH}$ = 6.1 Hz, $^4J_{PH}$ = 1.1 Hz, 2H, CH_2), 5.94 (t, $^3J_{HH}$ = 6.1 Hz, 1H, N*H*), 6.89 (ddd, $J \approx 7.7$, 4.6, 1.4 Hz, 1H, C_6H_4), 7.18 (td, $J \approx 7.5$, 1.5 Hz, 1H, C_6H_4), 7.24–7.38 (m, 21H, C_6H_4 and 2× P*Ph*$_2$), 7.51 (ddd, $J \approx 7.7$, 4.4, 1.3 Hz, 1H, C_6H_4). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 42.20 (d, $^3J_{PC}$ = 21 Hz, *C*H$_2$), 69.10 (fc *C*H), 71.63 (fc *C*H), 72.90 (d, J_{PC} = 4 Hz, fc *C*H), 74.12 (d, J_{PC} = 14 Hz, fc *C*H), 75.04 (d, $^1J_{PC}$ = 14 Hz, fc *C*-P), 76.46 (fc *C*-CONH), 127.83 (C_6H_4 *C*H), 128.21 (d, $^3J_{PC}$ = 7 Hz, PPh$_2$ *C*H$_m$), 128.70 (d, $^3J_{PC}$ = 8 Hz, PPh$_2$ *C*H$_m$), 128.80, 129.04 (2×PPh$_2$ *C*H$_p$); 129.42 (C_6H_4 *C*H), 129.80 (d, J_{PC} = 5 Hz, C_6H_4 *C*H), 133.43, 133.93 (2×$^2J_{PC}$ = 20 Hz, PPh$_2$ *C*H$_o$); 135.54 (d, J_{PC} = 13 Hz, C_6H_4 *C*$_{ipso}$), 136.03, 138.54 (2×$^1J_{PC}$ = 10 Hz, PPh$_2$ *C*$_{ipso}$); 142.78 (d, J_{PC} = 24 Hz, C_6H_4 *C*$_{ipso}$), 169.34 (*C*ONH). One signal due to *C*H of C_6H_4 was not clearly identified, being probably obscured by the resonance of the PPh_2 group (δ ca. 133.5). ^{31}P NMR ($CDCl_3$): δ −14.7 (s), −17.0 (s). IR (Nujol): ν/cm^{-1} 3239 (br m, ν_{NH}), 1742 (w), 1632 (vs, amide I), 1553 (vs, amide II), 1435 (s), 1311 (s), 1269 (m), 1194 (w), 1179 (m), 1161 (m), 1092 (w), 1030 (m), 833 (m), 748 (vs), 742 (vs), 697 (vs), 504 (s), 480 (m), 452 (m) cm^{-1}. Anal. Calc. for $C_{42}H_{35}FeNOP_2$ (687.5): C, 73.37; H, 5.13; N. 2.04. Found: C, 72.99; H, 5.08; N, 1.92%.

4.3. Preparation of complex **2**

Route A: [$PdCl_2$(cod)] (7.1 mg, 25 μmol) and **1** (17.2 mg, 25 μmol) were dissolved in dichloromethane (3 mL). The resulting solution was stirred for 45 min and filtered through a PTFE syringe filter (0.45 μm pore size). The filtrate was layered with hexane and the mixture was allowed to crystallise at −18 °C for several days. The separated crystalline product was filtered off, washed with hexane and dried in air to afford **2**·2CH_2Cl_2 as red crystals. Yield: 14 mg (54%).

^{1}H NMR ($CDCl_3$): δ 4.34 (apparent t, J = 1.9 Hz, 2 H, fc), 4.54 (br s, 2H, fc), 4.64 (m, 2 H, fc), 4.94 (d, $^3J_{HH}$ = 4.6 Hz, 2 H, NHCH_2), 5.21 (m, 2 H, fc), 6.82 (m, 1 H, C_6H_4), 7.23 (m, 1 H, C_6H_4), 7.32–7.75 (m, 22 H, C_6H_4 and P*Ph*$_2$), 7.80 (t, $^3J_{HH}$ = 4.6 Hz, 1 H, N*H*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 12.2 and 18.2 (2× d, $^2J_{PP}$ = 572 Hz). IR (Nujol): ν/cm^{-1} 3341 (w, ν_{NH}), 1652 (s, amide I), 1635 (vs, amide I), 1525 (vs, amide II), 1481 (m), 1434 (vs), 1306 (m), 1277 (s), 1198 (w), 1184 (m), 1168 (m), 1095 (s), 1037 (m), 1026 (m), 831 (m), 767 (s), 748 (vs), 692 (vs), 516 (vs), 503 (s), 468 (m). FAB+ MS: *m*/*z* 865 (M^+), 828 ([M−Cl]$^+$), 792 ([M−2Cl−H]$^+$), 737 (elemental composition of the fragments was confirmed by a comparison of experimental and theoretical isotopic patterns). Anal. Calc. for $C_{42}H_{35}P_2FePdCl_2NO$·2$CH_2Cl_2$ (1034.7): C, 51.07; H, 3.80; N, 1.35. Found: C, 51.30; H, 3.62; N, 1.27%.

Route B: [{Pd(μ-Cl)Cl(PMe_3)}$_2$] 6.6 mg (13 μmmol) and **1** (9.0 mg, 0.013 μmol) were dissolved in dichloromethane (2 mL). The resulting solution was stirred for 1 h, filtered (PTFE 0.45 μm) and then evaporated under reduced pressure. NMR analysis showed the presence of complex **2** contaminated with minor amounts of [$PdCl_2$(PMe_3)$_2$], analysing as follows: ^{1}H NMR ($CDCl_3$): δ 1.46 (d, $^2J_{PH}$ = 3.6 Hz, P*Me*$_3$); ^{31}P{^{1}H} NMR ($CDCl_3$): δ −10.6 (s).

4.4. Preparation of complex **3**

Route A: [PdCl(Me)(cod)] (14.7 mg, 50 μmol) and **1** (34.4 mg, 50 μmol) were dissolved in dichloromethane (5 mL). The mixture was stirred for 45 min and filtered (PTFE syringe filter, 0.45 μm pore size). Subsequent layering with hexane and crystallisation at −18 °C for several days gave the product as an orange solid, which was filtered off, washed with hexane and dried under vacuum. Yield of **3**·1/2CH_2Cl_2: 31 mg (70%).

Route B: [{Pd(μ-Cl)(Me)(PMe_3)}$_2$] (11.7 mg, 25 μmol) and **1** (17.2 mg, 25 μmol) were dissolved in dichloromethane (3 mL). The resulting solution was stirred for 1 h, filtered (PTFE syringe filter), and the filtrate layered with hexane. Crystallisation by diffusion at −18 °C for several days afforded the product as orange crystals, which were filtered off, washed with hexane and dried in air. Yield of **3**·1/2CH_2Cl_2: 14 mg (63%).

Analytical data for **3**·1/2CH_2Cl_2. ^{1}H NMR ($CDCl_3$): δ 0.10 (t, $^3J_{PH}$ = 6.1 Hz, 3 H, PdCH_3), 3.77 (br s, 1 H, fc), 4.07 (m, 1 H, fc), 4.23 (br s, 1 H, fc), 4.31, 4.43 (2× m, 1 H, fc), 4.68 (d, $^2J_{HH}$ = 13.8 Hz, 1 H, NHCH_2), 4.74, 5.02 (2× m, 1 H, fc), 5.09 (br dd, $^2J_{HH}$ = 13.8 Hz, $^3J_{HH}$ ca. 8.5 Hz, 1 H, NHCH_2), 5.85 (m, 1 H, fc), 6.93, 7.11 (2× m, 1 H, C_6H_4), 7.22–7.62 (m, 20 H, 2× P*Ph*$_2$), 8.07 (m, 2 H, C_6H_4), 8.31 (d, $^3J_{HH}$ ca. 8.5 Hz, 1 H, N*H*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 14.6 and 23.2 (2× d, $^2J_{PP}$ = 437 Hz). IR (Nujol): ν/cm^{-1} 3300 (w, ν_{NH}), 1649 (s, amide I), 1626 (vs, amide I), 1524 (vs, amide II), 1479 (m), 1436 (s), 1306 (w), 1281 (m), 1199 (w), 1185 (m), 1164 (w), 1102 (w), 1087 (m), 1030 (w), 844 (w), 832 (w), 761 (s), 746 (vs), 694 (s), 516 (vs), 507 (vs), 501 (s), 469 (m). Anal. Calc. for $C_{43}H_{38}P_2FePdClNO$·1/2CH_2Cl_2 (886.8): C, 58.91; H, 4.43; N. 1.58. Found: C, 59.04; H, 4.53; N, 1.54%.

4.5. Preparation of complex **4**

[{Pd(μ-Cl)Cl(PBu_3)}$_2$] (9.9 mg, 13 μmol) and **1** (9.0 mg, 13 μmol) were dissolved in dichloromethane (2 mL). The resulting solution was stirred for 1 h, filtered (PTFE 0.45 μm syringe filter) and then evaporated under reduced pressure leaving **4** as a yellow orange solid. Yield: 19 mg (quantitative).

^{1}H NMR ($CDCl_3$): δ 0.91, 0.94 (2× t, $^3J_{HH} \approx 7.5$ Hz, 18 H, *Me* of PBu_3), 1.38–1.70 (m, 24 H, β- and γ-CH_2 of PBu_3), 1.90–1.98 (m, 12 H, α-CH_2 of PBu_3), 4.35 (m, 2 H, fc), 4.57 (apparent q, $J \approx 2$ Hz, 2 H, fc), 4.69, 4.79 (2× apparent t, $J \approx 2$ Hz, 2 H, fc); 5.04 (d, $^3J_{HH}$ = 6.2 Hz, 2 H, NHCH_2), 6.85, 7.16 (2× m, 1 H, C_6H_4); 7.19 (t, $^3J_{HH}$ = 6.2 Hz, 1 H, N*H*), 7.32–7.70 (m, 22 H, C_6H_4 and P*Ph*$_2$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 12.0 (d, $^2J_{PP}$ = 558 Hz), 14.0 (d, $^2J_{PP}$ = 531 Hz), 17.5 (d, $^2J_{PP}$ = 558 Hz), 20.3 (d, $^2J_{PP}$ = 531 Hz). IR (Nujol): ν/cm^{-1} 3346 (w, ν_{NH}), 1657 (s, amide I), 1518 (s, amide II), 1435 (vs), 1302 (m), 1277 (m), 1166 (m), 1093 (m), 1029 (m), 999 (w), 967 (w), 903 (m), 744 (s), 693 (vs), 503 (composite s), 467 (m). ESI+ MS: *m*/*z* 1374 ([Pd_2(PBu_3)$_2$$Cl_2$(**1**)−H]$^+$); the observed isotopic distribution agreed to the calculated one. Anal. Calc. for

$C_{66}H_{89}Cl_4FeNOP_4Pd_2$ (1446.7): C, 54.79; H, 6.20; N, 0.97. Found: C, 54.98; H, 6.28; N, 0.97%.

4.6. Preparation of complex **5**

Di-μ-chlorido-bis{2-[(dimethylamino-κ*N*)methyl]phenyl-κC^1}-dipalladium(II) (13.8 mg, 25 μmol) and **1** (17.2 mg, 25 μmol) were dissolved in dichloromethane (3 mL). The solution was stirred under argon for 1 h and filtered (0.45 μm PTFE filter). The filtrate was layered with hexane and the mixture was crystallised by diffusion at 4 °C. Orange microcrystalline solid that separated during several days was filtered off, washed with hexane and dried under vacuum to afford **5** as an orange solid. Yield: 29 mg (93%).

^{1}H NMR ($CDCl_3$): δ 2.84 (apparent t, $^4J_{PH}$ = 2.6 Hz, 12 H, N*Me*$_2$), 4.07 (br s, 2 H, C*H*$_2$NMe$_2$), 4.12 (d, $^4J_{PH}$ = 1.9 Hz, 2 H, C*H*$_2$NMe$_2$), 4.36 (m, 2 H, fc), 4.41 (apparent q, $J \approx 2$ Hz, 2 H, fc), 4.75, 4.84 (2× apparent t, $J \approx 2$ Hz, 2 H, fc), 4.88 (d, $^3J_{HH}$ = 6.1 Hz, 2 H, NHC*H*$_2$), 6.22–6.48 (m, 4 H, C_6H_4), 6.78–7.76 (m, 30 H, C_6H_4, and 2× P*Ph*$_2$), 7.78 (t, $^3J_{HH}$ = 6.1 Hz, 1 H, N*H*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 33.2, 36.1 (2× s, *P*Ph$_2$). IR (Nujol): ν/cm^{-1} 3294 (w, ν_{NH}), 1654 (s, amide I), 1580 (w), 1525 (s, amide II), 1436 (vs), 1304 (m), 1279 (m), 1166 (m), 1096 (m), 1026 (m), 997 (w), 973 (w), 844 (m), 744 (vs), 694 (vs), 533 (s), 515 (s), 490 (m), 477 (m). ESI+MS: *m*/*z* 1168 ([Pd$_2$(L^{NC})$_2$(**1**)−H]$^+$; the observed isotopic distribution corresponded with the calculated one. Anal. Calc. for $C_{60}H_{59}Cl_2FeN_3OP_2Pd_2$ (1239.6): C, 58.13; H, 4.80; N, 3.39. Found: C, 57.82; H, 4.92; N, 3.29%.

4.7. General procedure for the Suzuki–Miyaura reaction

Aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), and complex **2** (5.0 μmol) or, alternatively, ligand **1** (5.0 μmol) and $Pd(OAc)_2$ (5.0 μmol) were mixed with dioxane (6 mL) under an argon atmosphere. The mixture was transferred to an oil bath preheated to 90 °C and stirred for 18 h. The mixture was cooled to room temperature, filtered (0.45 μm PTFE syringe filter), and the conversion was determined by ^{1}H NMR spectroscopy. The poisoning tests were performed in exactly the same manner (with **7d** as the substrate) except that mercury (1 mL) was introduced after 5 min of the reaction time.

4.8. X-ray crystallography

Single-crystals of **2**·1.25 $CHCl_3$ suitable for X-ray diffraction analysis were grown by recrystallisation from chloroform-hexane (orange plate, 0.03 × 0.18 × 0.42 mm^3). Full-set diffraction data (±*h* ± *k* ± *l*; 2θ ⩽ 55°) were collected on a Nonius KappaCCD diffractometer equipped with a Cryostream Cooler (Oxford Cryosystems) at 150(2) K using graphite monochromatised Mo Kα radiation (λ = 0.71073 Å) and analysed with the HKL program package [26]. The data were corrected for absorption by using a gaussian integration method based on the indexed crystal shape included in the diffractometer software [μ(Mo Kα) = 1.212 mm^{-1}, transmission factor range: 0.568–0.829].

The phase problem was solved by direct methods (SIR97 [27]) and the structure was refined by full-matrix least squares procedure based on F^2 (SHELXL97 [28]). The non-hydrogen atoms were refined with anisotropic thermal motion parameters. The amide hydrogen atom (H1N) was identified on a difference density map and refined as a riding atom. All other hydrogen atoms were included in the calculated positions and refined as riding atoms with U_{iso}(H). Geometric parameters and structural drawings were obtained with a recent version of PLATON program [29]. All numerical values are rounded with respect to their estimated standard deviations (esd's) given with one decimal; parameters involving fixed hydrogen atoms are given without esd's.

Crystallographic data: $C_{43.25}H_{36.25}Cl_{5.75}FeNOP_2Pd$ (**2**·1.25$CHCl_3$), M = 1014.01 g mol^{-1}, monoclinic, space group $P2_1/n$ (no. 14), a = 11.5783(2), b = 14.4658(2), c = 26.3293(4) Å; β = 100.3694(9)°, V = 4337.9(1) Å^3, Z = 4, D = 1.553 g mL^{-1}, 62 684 diffractions of which 9893 were unique and 8578 observed according to $I_o > 2\sigma(I_o)$ criterion, R_{int} = 5.00%; 510 parameters, R(observed diffractions) = 3.98%, R(all data) = 4.78%, wR(all data) = 11.67%, residual electron density: 1.56, −1.38 e Å^{-3} (the largest electron peak and hole are located in the space accommodating the disordered solvate molecules).

5. Supplementary material

CCDC 714155 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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