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Pd(II) Complexes with Chelating Phosphinoferrocene Diaminocarbene Ligands: Synthesis, Characterization, and Catalytic Use in Pd-Catalyzed Borylation of Aryl Bromides

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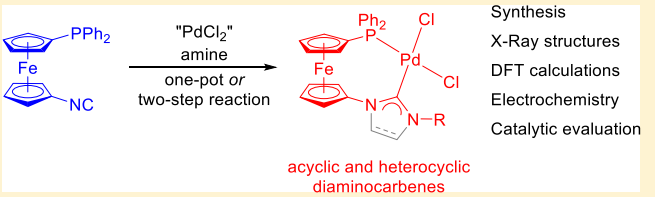
Supporting Information

ABSTRACT: We developed a novel, straightforward route toward Pd(II)-aminocarbene complexes bearing a P-chelating phosphinoferrocenyl substituent based on a three-component reaction of 1′-(diphenylphosphino)-1-isocyanoferrocene (**1**) with [$PdCl_2$(cod)] (cod = cycloocta-1,5-diene) and nucleophilic amines. Depending on the type of the amine, the reaction produced acyclic diaminocarbenes and their saturated (imidazolin-2-ylidene) and unsaturated (imidazol-2-ylidene) cyclic counterparts (NHCs). Using (*S*)-2-(chloromethyl)pyrrolidine as the nucleophile, this method afforded a separable pair of stable diastereomeric bicyclic imidazolin-2-ylidene carbenes with different configurations of the planar-chiral ferrocene unit. The prepared P-chelating carbenes were characterized using spectroscopic methods, X-ray crystallography, and DFT methods. The last were used to explain the formation of isomeric open diaminocarbenes featuring NHR groups at the wing-tip position, trends in Pd−Cl bond lengths reflecting similar *trans* influences of the particular carbene and phosphine donors, and the results from cyclic voltammetric measurements. Furthermore, the carbenes were used as defined (pre)catalysts in Miyaura borylation of aryl bromides with bis(pinacolato)diboron. When applying the optimized catalytic system (1 mol % Pd catalyst, KOAc as the base, 2-propanol, 85 °C), this reaction produced a range of simple and substituted arylboronate pinacol esters in high yield and without biaryl side products.

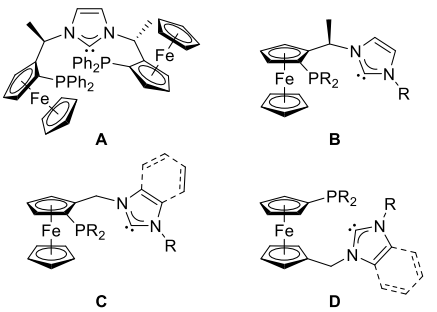


INTRODUCTION

The discovery of persistent carbenes and their transition metal complexes[1,2] has led to a remarkable paradigm shift in the design of ancillary ligands for transition metal chemistry and catalysis. In particular, N-heterocyclic carbenes (NHCs)[3] emerged as attractive alternatives to ubiquitous phosphine ligands. Similarly to phosphine donors, the coordination properties of NHCs can be easily varied by changing the organic scaffold and substituents and, thus, advantageously fine-tuned to a specific purpose.[4]

Perhaps unsurprisingly, research on NHCs has recently intertwined with the chemistry of ferrocene-based ligands, which is another rapidly developing research area.[5] Now, the use of ferrocene fragments in the design of NHCs is no longer uncommon, with applications ranging from mere pendant substituents to the very molecular scaffold and carriers of molecular chirality.[6] Among these applications, compounds featuring phosphinoferrocenyl substituents stand out for combining NHC (most typically an imidazol-2-ylidene) with phosphine donor moieties, in addition to their ability to form P,C-chelate complexes.[7] Representative examples of such compounds, **A**,[8] **B**,[9] **C**,[10] and **D**,[10a,11] shown in Chart 1,[12] have been synthesized using conventional methods, namely N-alkylation of suitable imidazoles with ferrocenylmethylating agents[13] followed by deprotonation of the resulting imidazolium salts.

Chart 1. Examples of Ferrocene Phosphino-NHC Ligands[a]



[a]The ligands are shown in their generic form with unspecified substituents R and, for **C**, also with unspecified planar chirality.

These compounds, however, inevitably contain methylene linking groups between the imidazolylidene fragment and the ferrocene group. We hypothesized that this type of compound albeit *without* a linker should be easily accessible through nucleophilic additions across coordinated isocyanides. Although this approach has been known for a century,[14] it has only been rarely used to prepare carbene complexes *with*

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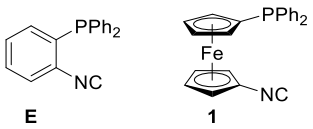
phosphine substituents,[15] primarily due to the lack of suitable synthetic precursors, i.e., phosphino-isocyanides.

Recently, Duan and Matthey[16] and our group[17] have reported the synthesis of the first phosphines bearing isocyanide substituents potentially suitable for the preparation of chelate complexes (compounds **E** and **1** in Chart 2). Having

Chart 2. Phosphino-Isocyanides Relevant to This Study

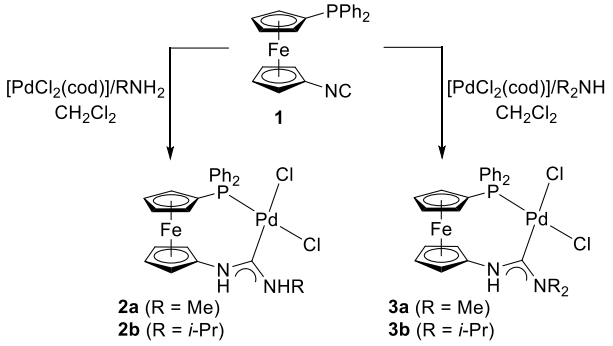


demonstrated that isocyanide **1** readily inserts into Pd−C bonds to produce Pd(II) imidoyl complexes,[18] we decided to extend our studies toward the synthesis of new phosphino-ferrocene−carbene complexes via reactions of Pd-**1** species with amine nucleophiles. Resulting from these efforts, this contribution describes the synthesis and structural characterization of open and cyclic diaminocarbene Pd(II) complexes and their application in Pd-catalyzed Miyaura borylation[19] of aryl bromides with bis(pinacolato)diboron.

RESULTS AND DISCUSSION

Syntheses. Repeated initial attempts to prepare *defined* Pd-**1** complexes (such as $PdCl_2(\mathbf{1})_n$) as starting materials for further reactivity studies failed, only resulting in ill-defined, dark, and insoluble (probably polymeric) materials. Hence, we resorted to a one-pot approach based on a simultaneous addition of a Pd precursor and an amine to **1**.[20] Indeed, the reaction of **1** with $[PdCl_2(cod)]$ (cod = cycloocta-1,5-diene) and with a slight excess of primary ($MeNH_2$, *i*-$PrNH_2$) and secondary (Me_2NH, *i*-Pr_2NH) amines produced acyclic diaminocarbenes **2** and **3** in moderate-to-good yields (35−64%; isopropyl-substituted amines gave consistently better yields) after chromatographic purification (Scheme 1). In

Scheme 1. Synthesis of Acyclic Carbenes 2 and 3[a]

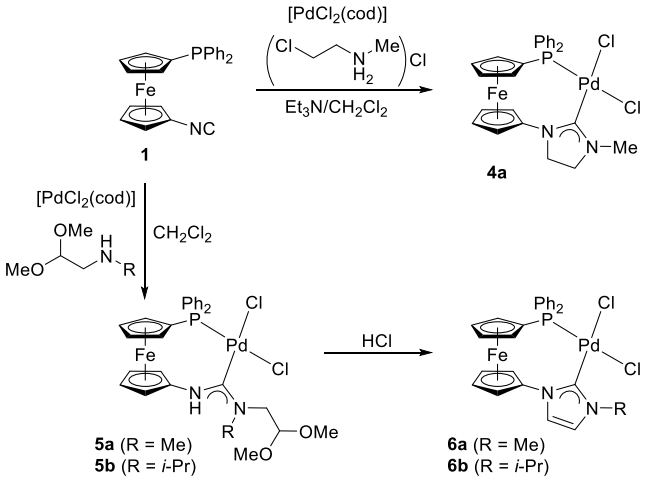


[a]cod = cycloocta-1,5-diene.

particular, the reaction with methylamine afforded the diprotic carbene **2a** as a mixture of two isomers[21b] (*vide infra*) in a ratio of approximately 2:1, whereas a similar reaction with isopropylamine produced carbene **2b** as a single isomer. The reactions with dimethylamine (generated *in situ* from $Me_2NH\cdot HCl$ and NEt_3) and with diisopropylamine furnished the respective monoprotic carbenes **3a** and **3b**.

The analogous imidazolin-2-ylidene carbene **4a** resulted from the reaction of $[PdCl_2(cod)]$/**1** with *N*-(2-chloroethyl)-methylamine generated *in situ* from the corresponding hydrochloride and triethylamine (Scheme 2). In this reaction,

Scheme 2. Synthesis of Cyclic Carbenes 4 and 6[a]



[a]cod = cycloocta-1,5-diene.

the base additive (NEt_3), used in excess, facilitates intramolecular alkylation in the intermediate carbene which closes the imidazoline ring.[21] However, this transformation proved rather delicate. Although the reaction with $[(ClCH_2CH_2)NH_2Me]Cl/NEt_3$ produced imidazolin-2-ylidene carbene **4a** in a 85% isolated yield, we were unable to isolate a similar product from the reaction with the bulkier (2-chloroethyl)-isopropylamine. The reaction most likely proceeded as expected but mainly produced other unidentified products that could not be separated from the desired carbene complex.

Ultimately, imidazol-2-ylidene complexes **6** were prepared analogously, using amino acetals $(MeO)_2CHCH_2NHR$ (R = Me, *i*-Pr) as protected building blocks (nucleophiles).[22] In the first step, the reaction of the acetals with $[PdCl_2(cod)]$/**1** produced stable acyclic carbenes **5** in good yields (Scheme 2). Similarly to the **2a** and **2b** pair, compound **5a** was isolated as a mixture of isomers[21b] (≈2:1 ratio, 85% overall yield), whereas **5b** was isolated as a single isomer (73%). After adding HCl (in dioxane) to dichloromethane solutions of **5**, these diamino-carbenes smoothly transformed into the corresponding imidazol-2-ylidene complexes **6a** and **6b**, which were isolated by column chromatography at yields exceeding 90%. Bulky ($AdaNH_2$, $AdaNHCH_2CH_2Cl$, and $AdaNHCH_2CH(OMe)_2$; Ada = 1-adamantyl) and the less nucleophilic aromatic ($MesNH_2$, $MesNHCH_2CH_2Cl$, and $MesNHCH_2CH(OMe)_2$; Mes = mesityl) amines did not react or produced complex mixtures under similar reaction conditions.

Structural Characterization. NMR spectra of the isolated compounds were fully consistent with the formulation. Diagnostic $^{13}C\{^1H\}$ NMR resonances (Table 1) due to carbene carbons were observed as ^{31}P-coupled doublets at δ_C 193−200 for acyclic and imidazolin-2-ylidene carbenes, whereas those of imidazol-2-ylidene complexes **6** appeared at higher fields ($\delta_C \approx 164$) and showed no interactions with the phosphorus atom in the *cis* position. The ferrocene moieties gave rise to eight separate CH resonances in both ^1H and ^{13}C NMR spectra of all compounds, thus suggesting that the

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Table 1. Selected Spectroscopic Data for Carbenes 2−6[a]

carbene	$\nu_{carbene}$	δ_C [$^2J_{PC}$]	δ_P
2a	1581	199.8, 191.9[b]	17.8, 17.7
2b	1570	193.45 [6]	17.8
3a	1572	194.55 [7]	17.9
3b	1546	193.19 [8]	16.3
5a	1560	196.25 [7], 198.43 [7]	18.0, 17.2
5b	1547	197.49 [8]	16.8
4a	1541, 1497	194.68 [2]	18.4
6a	1571, 1497	164.76	17.2
6b	1541, 1492	162.68	18.1

[a] $\nu_{carbene}$ = frequencies of carbene bands (in cm^{-1}) in IR spectra recorded in Nujol mulls, δ_C = chemical shift of the carbene carbon (in ppm) and $^2J_{PC}$ coupling constants (in Hz), when observed, δ_P = ^{31}P NMR shifts (in ppm). For solubility reasons, the NMR spectra were recorded in CD_2Cl_2−CD_3OD. [b] Chemical shifts from 2D spectra.

ferrocene moieties had fixed conformations, which render their CH groups diastereotopic. In addition, pairs of ^1H NMR signals attributable to protons in the α-position of the cyclopentadienyl rings were observed at markedly lower fields (up to $\delta_H \approx 6$), presumably due to shielding anisotropy. $^{31}P\{^1H\}$ NMR signals occurred at δ_P 16−18.

Complexes **2**−**6** displayed IR bands attributable to carbene ν_{NCN} vibrations in the range 1490−1580 cm^{-1} (see Table 1), in addition to ν_{NH} bands above 3000 cm^{-1} in the protic carbenes. In electrospray ionization (ESI) mass spectra, they showed ions resulting from the $[M - Cl]^+$ and/or $[M - HCl - Cl]^+$ fragments.

The structures of compounds **2b**, **3a**, **3b**, **4a**, **5b**, **6a**, and **6b** were determined by single-crystal X-ray diffraction analysis, often in solvated form (see the Experimental Section). Molecular diagrams are shown in Figure 1, and pertinent geometric data are outlined in Table 2. Additional structural diagrams are available in the Supporting Information.

The coordination planes, {PdP(C)Cl_2}, in all structurally characterized compounds are distorted from the ideal square-planar geometry for two main reasons. First, the coordination bonds to carbene carbons are substantially shorter than the bonds to the remaining donor atoms. Second, the interligand angles slightly depart from the ideal 90° (by maximum ±5°), thus reflecting the spatial congestion and steric demands of the chelating phosphinocarbene ligands (N.B. the bite angles associated with the P-chelating aminocarbene ligands fall in the rather narrow range 86−90°).

The carbene planes, {N1, C11, N2}, are oriented nearly perpendicularly to the coordination plane (the interplanar angles φ are ≈80°; see Table 2), and the N1−C11−N2 angles decrease from open carbenes through cyclic imidazolin-2-ylidene to their imidazol-2-ylidene counterparts (N.B. the N−C−N angles of cyclic carbenes are similar to those determined for the respective free ligands).[23] The saturated C_3N_2 ring in the structure of **4a** is twisted at the C12−C13 bond (the torsion angle N1−C12−C13−N2 is 8.4(3)°), whereas the unsaturated carbene rings in **6a** and **6b** are planar and delocalized. The bridging ferrocene units are only marginally tilted (by ≈3−6° in the series). To facilitate chelate coordination, the substituents at the cyclopentadienyl rings are nearly eclipsed (τ = 5−13°), and the attached NCN moieties are rotated by ≈40° from the planes of their parent cyclopentadienyl rings (see ψ angles in Table 2).

Another noteworthy feature is the variability in Pd−Cl bond lengths. Pd−Cl2 bonds located *trans* to the carbene in the *open* diaminocarbenes are slightly but statistically significantly longer than Pd−Cl1 bonds *trans* to the phosphine moiety, whereas the opposite is found in the structures of the *cyclic* carbenes **4a**, **6a**, and **6b**. This observation is in line with the notion that the *trans* influence of phosphines is similar to that of NHC carbenes based on both structural[24] and reactivity[9c] data. Otherwise, however, Pd-donor distances match the data reported for complexes with **C**-type ligands, $[PdCl_2(\mathbf{C}\text{-}\kappa^2P,C)]$.[10b,c]

The fact that compound **2b**, isolated as a single isomer, according to NMR analysis, was structurally characterized as the seemingly more sterically crowded *anti* isomer bond led us to further analyze its solid-state structure and, especially, to compare the DFT-computed energies and structures of both isomers of open carbenes **2** (see Chart 3). Three different functionals (B3LYP, PBE0, and TPSS), used to eliminate a possible bias, consistently indicated that the *syn* isomers of **2a** and **2b** are energetically favored and that the energy difference between the isomers is significantly larger in compound **2b** featuring the bulkier terminal substituent (Table 3) than in compound **2a**.

The computed structure of *syn*-**2b** differed only marginally from that determined in the solid state, thereby validating our approach (the average absolute deviation from experimental bonds distances was 0.056 Å, with a maximum of 0.138 Å for the N(*i*-Pr)-H bond). Because the NCN moieties are rotated with respect to the coordination planes (*vide supra*), the isopropyl substituent is positioned above the coordination

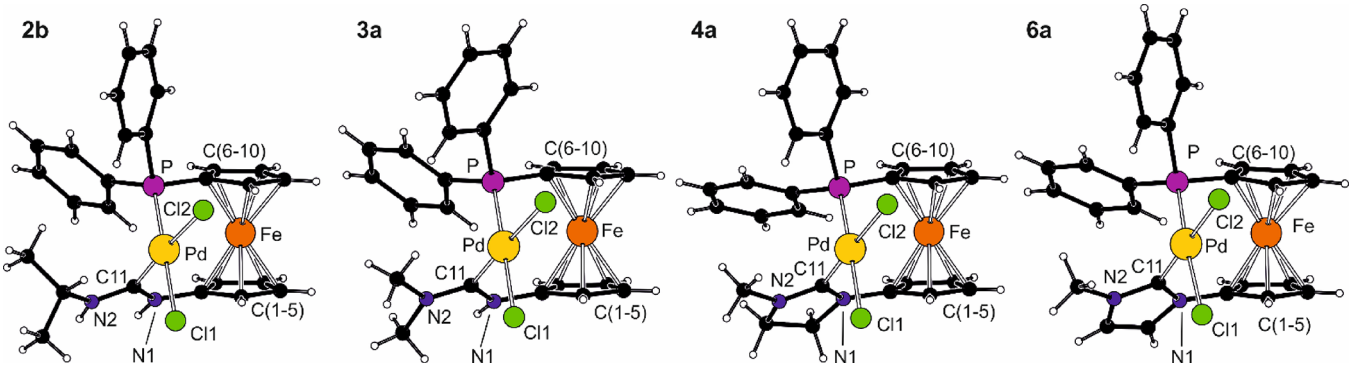

Figure 1. Views of the molecular structures of representative carbene complexes **2b** (molecule 1), **3a**, **4a**, and **6a** (further structural diagrams are available in the Supporting Information).

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Table 2. Selected Distances and Angles of Structurally Characterized Carbene Complexes[a]

parameter	2b·xCHCl3		3a·2CHCl3	3b·CHCl3·AcOEt	4a·2MeOH	5b·CH2Cl2		6a·2CH2Cl2	6b·1.75CH2Cl2	
	mol 1	mol 2				mol 1	mol 2		mol 1	mol 2
Pd–Cl1	2.373(1)	2.366(1)	2.3634(7)	2.3656(7)	2.3832(8)	2.356(1)	2.353(1)	2.3631(7)	2.370(1)	2.3774(9)
Pd–Cl2	2.3911(9)	2.371(1)	2.3772(5)	2.3668(7)	2.3552(8)	2.3743(9)	2.3745(9)	2.3455(8)	2.3498(9)	2.3409(8)
Pd–P	2.265(1)	2.2452(9)	2.2480(5)	2.2593(7)	2.2514(8)	2.263(1)	2.258(1)	2.2385(7)	2.2399(6)	2.2592(7)
Pd–C11	1.968(3)	1.969(4)	1.975(2)	1.987(2)	1.958(3)	1.985(3)	1.981(3)	1.976(3)	1.974(3)	1.967(3)
C11–N1	1.333(3)	1.338(5)	1.344(2)	1.339(3)	1.342(4)	1.335(4)	1.341(4)	1.357(3)	1.352(4)	1.354(4)
C11–N2	1.319(4)	1.321(3)	1.325(3)	1.332(3)	1.323(3)	1.329(4)	1.332(4)	1.335(3)	1.343(4)	1.343(3)
N1–C11–N2	116.5(3)	116.1(3)	117.6(2)	119.4(2)	109.7(2)	118.2(3)	118.6(3)	105.8(2)	105.8(3)	105.7(2)
Cl1–Pd–Cl2	90.51(4)	90.81(3)	90.94(2)	90.41(3)	91.66(3)	90.88(3)	91.42(3)	91.18(3)	91.58(3)	92.22(3)
P–Pd–C11	89.7(1)	89.96(8)	89.74(6)	90.51(7)	86.27(8)	90.3(1)	90.0(1)	87.54(7)	88.07(7)	89.50(9)
∠Cl1, Cp2	3.1(2)	3.6(3)	3.4(1)	4.2(2)	3.0(2)	5.7(2)	5.3(2)	4.8(2)	5.1(2)	4.9(2)
τ	8.4(3)	12.5(2)	10.3(1)	−9.3(2)	−6.8(2)	−9.9(2)	−8.8(2)	5.2(2)	−7.0(2)	7.4(2)
φ	78.1(4)	84.6(3)	80.3(2)	79.3(3)	78.0(3)	83.1(4)	82.1(4)	83.3(2)	84.2(2)	78.0(3)
ψ	44.4(4)	40.7(3)	42.7(2)	41.4(3)	39.9(3)	42.5(4)	41.9(4)	44.4(2)	44.6(2)	43.9(3)

[a]Definitions: Cp1 and Cp2 are the cyclopentadienyl rings C(1−5) and C(6−10), respectively. Cg 1 and Cg2 denote their respective centroids. τ is the torsion angle C1−Cg2−Cg2−C6. φ is the dihedral angle subtended by the plane {N1, C11, N2} and by the coordination plane {Pd, Cl1, Cl2, P, C11}, and ψ is the dihedral angle between the plane {N1, C11, N2} and by the cyclopentadienyl ring Cp1.

Chart 3. Isomers of Acyclic Carbenes 2

[a]The adopted prefixes relate to the relationship between the terminal substituents R and the central Pd−C bond (R = Me, *i*-Pr).

Table 3. Free Energy Differences (ΔG at 298 K in kcal mol^{-1}) Between the Isomers of Complexes 2a and 2b Calculated Using Three Different DFT Functionals[a]

compound	ΔG(B3LYP)	ΔG(PBE0)	ΔG(TPSS)
***syn*-2a**/*anti*-**2a**	−0.1	−0.1	+0.1
***syn*-2b**/*anti*-**2b**	−0.8	−0.8	−1.5

[a]Calculated with the specified functionals at the def2-TZVP:cdd-(Fe,Pd)-D3 level of theory. Solvent effects (dichloromethane) have been approximated using the PCM model. For details, see the Experimental Section and the Supporting Information. The preferred isomer is indicated in bold.

plane in the structure of *syn*-**2b**, with one of its CH hydrogens directed toward the palladium and with the methyl groups extending away from the central atom, without much crowding. One of the methyl groups is oriented to form supportive intramolecular C−H···Cl contacts, as observed in the solid-state structure (molecule 2: C63···Cl21 = 3.680(4) Å, angle at H = 147°) and further confirmed by AIM analysis (a bond critical point with hydrogen-bond characteristics, according to the Koch−Popelier definition, was located between the hydrogen atom of the CH_3 group and the Pd-bound chloride[25]). Conversely, the analysis of DFT-optimized structural data and calculated parameters of the *anti* isomer revealed the lack of such stabilizing interaction and suggested possible steric crowding between the methyl groups and a phenyl substituent (Figure 2). In addition, the *syn* isomers in

Figure 2. Space filling diagrams for DFT-optimized structures of *syn*- and *anti*-**2b**, as viewed perpendicularly to the coordination plane (top) and along the C11−Pd bond (bottom); note: the color code is the same as that used in Figure 1.

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which both NH hydrogens point away from the central Pd-carbene bond can experience additional stabilization in the *solid state* through cooperative hydrogen bonds, as shown in the crystal structure of *syn*-**2b** (see Figure 3).

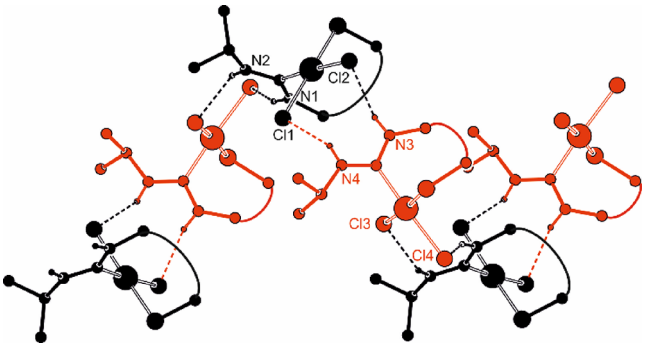
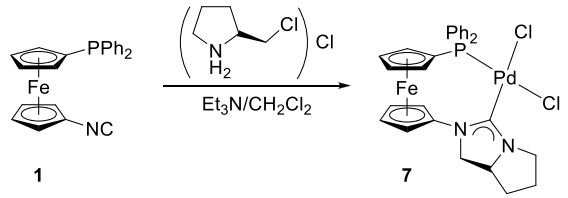


Figure 3. Simplified view of H-bonded chains in the structure of solvated **2b**; for clarity, the phenyl rings and CH hydrogens are omitted, and the bulky ferrocene units are replaced with ribbons connecting pivotal atoms (molecule 1 in black, molecule 2 in red). Hydrogen bond lengths (in Å): N1···Cl4, 3.283(3); N2···Cl3, 3.204(3); N3···Cl12, 3.169(3); N4···Cl1, 3.207(3).

Preparation of Chiral Carbene 7. To extend our synthetic endeavors, we used the fixed geometry of the ferrocene core to prepare an optically pure P-chelated carbene complex. For this purpose, we treated [$PdCl_2$(cod)]/**1** with (*S*)-2-(chloromethyl)pyrrolidine, which is accessible from (*S*)-proline.[26] Gratifyingly, this reaction proceeded as expected (Scheme 3), producing bicyclic carbene **7** as a mixture of

Scheme 3. Synthesis of Chiral Carbene 7[a]



[a]cod = cycloocta-1,5-diene.

diastereoisomers in a 3:2 ratio and 65% overall yield. We were able to separate the isomers by chromatography and to structurally authenticate the major product as (S,R_p)-**7** by X-ray diffraction analysis (*vide infra*).

The diastereoisomers could be clearly distinguished by their NMR spectra (see the Supporting Information); the diagnostic carbene ^{13}C NMR and the ^{31}P NMR signals were identified at δ_C 198.08/190.88 and at δ_P 18.8/16.3 for (S,R_p)-**7** and (S,S_p)-**7**, respectively. However, the fact that the isomers differ in configuration at the planar-chiral ferrocene unit was more clearly expressed in electronic circular dichroism (ECD) spectra, showing a nearly (albeit not ideally, due to their diastereomeric relationship) mirror-symmetric response in the region dominated by ferrocene d−d transitions (Figure 4).[27]

The molecular structure of (S,R_p)-**7** is presented in Figure 5, along with selected structural parameters. The comparison of the parameters with the values derived from the aforementioned structures (Table 2) revealed only marginal differences, thus suggesting that the annelation of the carbene moiety has no significant impact on the overall structure. The five-membered ring around the carbene moiety, {N1, C11, N2, C12, C3}, is only marginally twisted (N1−C12−C13−N2 = 10.2(3)°; cf. the structure of **4a**), whereas the appended ring {N2, C13, C26−C28} adopts an approximate envelope conformation with the C26 atom at the tip position.[28]

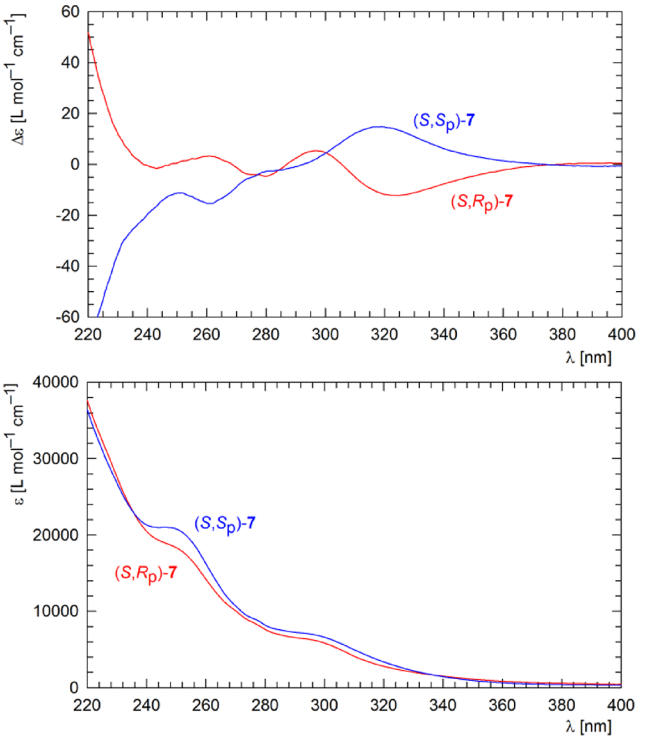


Figure 4. ECD (top) and UV−vis (bottom) and spectra of (S,R_p)-**7** (red line) and (S,S_p)-**7** (blue line).

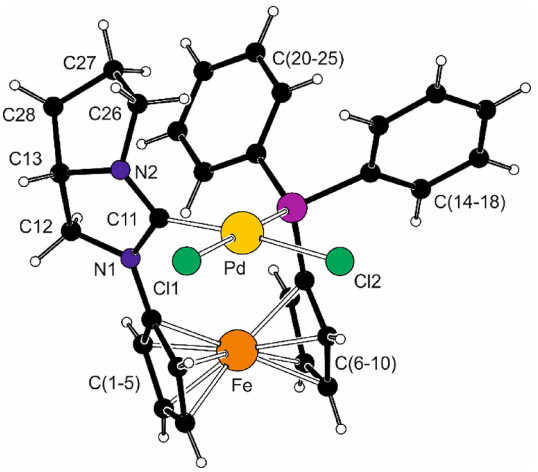


Figure 5. View of the molecular structure of (S,R_p)-**7**. Selected distances and angles (in Å and deg): Pd−Cl1, 2.3722(9); Pd−Cl2, 2.3532(8); Pd−P, 2.2559(8); Pd−C11, 1.962(3); Cl1−Pd−Cl2, 91.00(3); P−Pd−C11, 90.54(8); C11−N1, 1.348(4); C11−N2, 1.327(3); N1−C11−N2, 108.7(2); τ = 8.9(2), φ = 74.8(2), ψ = 45.7(3) (for definitions, see Table 2).

DFT Computations and Electrochemistry. In addition to explaining differences among isomers (*vide supra*), DFT computations (PBE0/def2-TZVP:sdd(Fe,Pd)-D3) were used to follow possible changes in bonding in the series of diaminocarbenes **3a**, **4a**, and **6a**. The inspection of frontier orbitals (Figure 6 and Figure S13) showed that the HOMO is

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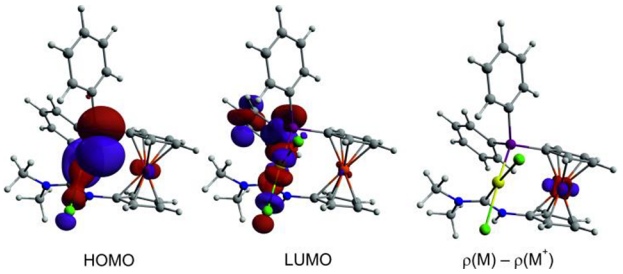


Figure 6. Frontier orbitals (isosurfaces at ±0.05 au) and electron density difference map, $\rho(M) - \rho(M^+)$, at the geometry of M (isosurfaces at ±0.02 au) for carbene complex **3a**. Diagrams for compounds **4a** and **6a** are presented in the Supporting Information.

mainly contributed from the chloride ligands (≈75%, mostly 3p orbitals, according to the NBO analysis), with a smaller contribution from Pd (≈10%) and P (≈4%). The contributions from the Fe orbitals ranged from 1% to 3%. Conversely, the LUMO orbitals were more delocalized and mainly consisted of the orbitals of one P−Ph moiety, of the palladium (15−20%), of the carbene carbon, and of chloride ligands.

DFT computations closely reproduced the observed variation in Pd−Cl bond lengths. However, these changes were not straightforwardly reflected in the electronic structure of the model carbenes **3a**, **4a**, and **6a**, particularly in the calculated electron density $\rho(r)$, in its Laplacian $\nabla^2\rho(r)$ and in bond ellipticity (ε) at bond critical points (see Table S2).[29] Nonetheless, the same parameters indicated that the carbene carbon was more strongly coordinated and with a more significant contribution of π-back bonding, as reflected by the higher ellipticity values for the Pd−C bonds, than the phosphorus atom.

Using the ferrocene moiety as a probe at the molecular level, we also studied the electrochemical behavior of representative carbenes **3a**, **4a**, and **6a** by cyclic (CV) voltammetry at the platinum disc electrode in dichloromethane. In the anodic region, these compounds displayed an electrochemically reversible redox change (Figure 7). Only for the open carbene **3a**, the redox wave was broader and asymmetric, presumably due to diminished reversibility and/or adsorption phenomena. The half-wave potentials determined from CV increased from

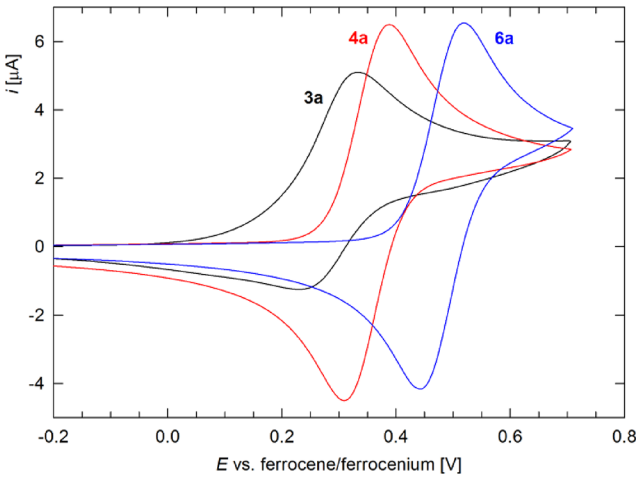


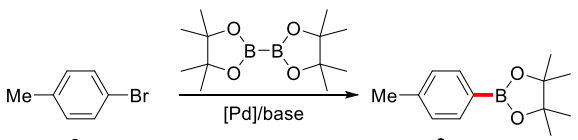
Figure 7. Cyclic voltammograms of **3a**, **4a**, and **6a** (recorded at the Pt disc electrode at the scan rate of 0.1 V s^{-1}); the potentials are expressed in relation to ferrocene/ferrocenium.

3a (0.28 V) through **4a** (0.35 V) to **6a** (0.48 V). This indicates not only an increase in the overall electron-withdrawing nature of the carbene substituents (in the same order), and consequently their lower donating ability,[4,30] but also the conjugated nature of the compounds, wherein differences in "substituent" are relayed to the central ferrocene core. Notably, all potentials were lower than that of [$PdCl_2$(dppf-κ^2P,P')] (0.58 V;[31] dppf = 1,1′-bis(diphenylphosphino)ferrocene) under similar conditions, thus attesting to the easier oxidation of carbene complexes and, hence, to the higher electron density at their ferrocene core.

Despite the dominant contribution of chlorine-based orbitals to the HOMO, the assignment of the observed redox transition as a standard one-electron oxidation of the ferrocene unit was corroborated by changes in DFT-computed electron density. For all studied compounds, the difference electron density, $\rho(M) - \rho(M^+)$, calculated for the molecule in its native state (M) and for the corresponding cation at the *same* geometry (M^+; the electron transfer is fast and precedes any possible structural change), suggested that the electron is almost exclusively removed from the ferrocene iron (see Figure 6 and Figure S13).

Catalytic Evaluation. The catalytic properties of Pd(II) complexes with phosphinoferrocene carbene ligands were examined in Pd-catalyzed Miyaura borylation of aryl bromides with bis(pinacolato)diboron.[19] This reaction, directly converting the ubiquitous starting materials into useful synthetic building blocks,[32] often employs dppf as the supporting ligand for palladium and, hence, allows comparisons in terms of catalyst efficiency. As a model reaction, we chose the borylation of 4-bromotoluene into ester **9a** and used the imidazole carbene **6b** as (pre)catalyst (Scheme 4).

Scheme 4. Testing Catalytic Reaction



Initial reaction tests revealed that strictly inert conditions (i.e., oven-dried glassware, dry base additives and solvent, and rigorous exclusion of air) are essential for obtaining boronate esters in good yields. The results from subsequent optimization experiments (Table 4) illustrate that the yield of boronate ester **9a** varies greatly in different solvents (Table 4, entries 1−6). When using potassium acetate, which is commonly applied in this reaction,[33] the best yield of **9a** was obtained in isopropanol, whose relative permittivity (ε_r) is approximately intermediate between those of toluene and DMSO, which represent the extreme cases among the tested solvents.[34] Lowering the amount of KOAc from 3 equiv to 2 equiv had no significant effect on the reaction yield; however, further decreasing this amount to 1.5 equiv lowered the yield to 92% (entries 3, 7, and 8). The survey of base additives (entries 3 and 9−14) also showed remarkable differences. For instance, the reaction in the presence of NaOAc proceeded with full conversion of the substrate **8a** but mainly produced (62%) 4,4′-dimethylbiphenyl as the "homocoupling" product. Stronger bases such as KOH and *t*-BuOK also activated the primary product **9a** toward Suzuki−Miyaura cross-coupling, producing 4,4′-dimethylbiphenyl. Conversely, less homocoupling product

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Table 4. Summary of the Optimization Experiments[a]

entry	solvent	base (equiv)	NMR yield[b] (%)
1	toluene	KOAc (3.0)	61(0)
2	1,4-dioxan	KOAc (3.0)	54(0)
3	*i*-PrOH	KOAc (3.0)	99(0)
4	MeCN	KOAc (3.0)	17(0)
5	DMF	KOAc (3.0)	27(0)
6	DMSO	KOAc (3.0)	31(0)
7	*i*-PrOH	KOAc (2.0)	98(0)
8	*i*-PrOH	KOAc (1.5)	92(0)
9	*i*-PrOH	NaOAc (2.0)	38(62)
10	*i*-PrOH	CsOAc (2.0)	95(1)
11	*i*-PrOH	K_2CO_3 (2.0)	76(9)
12	*i*-PrOH	K_3PO_4 (2.0)	92(7)
13	*i*-PrOH	KOH (2.0)	82(18)
14	*i*-PrOH	*t*-BuOK (2.0)	73(27)

[a]Conditions: 4-bromotoluene (1.0 mmol), bis(pinacolato)diboron (1.2 mmol), 1 mol % of **6b**, solvent (4 mL), 85 °C, 24 h. [b]NMR yields are an average of two independent runs. The yield of the homocoupling product (4,4′-dimethylbiphenyl) is given in parentheses.

was obtained in reactions with K_2CO_3, giving **9a** in a 76% yield, and with K_3PO_4 and CsOAc, which ensued in >90% yields of the boronate ester, with only minor amounts of the biphenyl (7% and 1%, respectively). Lastly, no reaction was observed when substrate **8a** was replaced by the corresponding chloride.

Subsequent experiments revealed significant differences between precatalysts (Table 5). Of the tested compounds, **4a**

Table 5. Comparison of the Precatalysts[a]

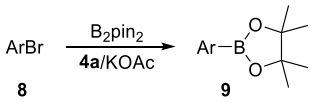
catalyst	NMR yield[b] (%)	catalyst	NMR yield[b] (%)
2a	89(6)	**4a**	98(0)
2b	77(3)	**6a**	91(2)
3a	88(3)	**6b**	98(0)
3b	98(1)	[$PdCl_2$(dppf)]	90(2)

[a]Conditions: 4-bromotoluene (1.0 mmol), bis(pinacolato)diboron (1.2 mmol), KOAc (2.0 mmol), 1 mol % of catalyst, *i*-PrOH (4 mL), 85 °C, 6 h. [b]NMR yields are an average of two independent runs. The yield of the homocoupling product (4,4′-dimethylbiphenyl) is given in parentheses.

and **6a** reacted selectively and achieved quantitative (within the margins of experimental error) yields of **9a** within 6 h of reaction. The efficiency of compound **3b** was close to those of **4a** and **6a**, albeit with minor amounts of 4,4′-dimethybiphenyl; the benchmark catalyst, [$PdCl_2$(dppf)], behaved very similarly. Other investigated phosphinocarbene complexes performed relatively worse, producing 77−91% of **9a** and 2−6% of the homocoupling product.

On the basis of the aforementioned results, the more easily accessible precatalyst **4a** was chosen for the following scope experiments. The reactions were performed in *i*-PrOH using KOAc as the base (2 equiv) at 85 °C for 6 h. The results outlined in Table 6 indicate that nonfunctionalized aryl halides react typically very well in the absence of pronounced steric crowding. Nonetheless, even mesityl bromide could be converted into the respective boronate ester **9d** with a 40% isolated yield when the reaction time was extended to 24 h. Among the functionalized aryl halides, the lowest yield of the coupling product was achieved when using *p*-anisyl bromide

Table 6. Reaction Scope Tests[a]



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substrate **8** (Ar in ArBr)	yield of **9** (%)	substrate **8** (Ar in ArBr)	yield of **9** (%)
4-tolyl (**a**)	94	4-C_6H_4OMe (**g**)	78
3-tolyl (**b**)	94	4-C_6H_4NHAc (**h**)	97
2-tolyl (**c**)	88	4-C_6H_4CHO (**i**)	92
mesityl (**d**)	40[b]	4-C_6H_4Cl (**j**)	85
1-naphthyl(**e**)	66	4-C_6H_4F (**k**)	95
2-naphthyl (**f**)	90	4-$C_6H_4CF_3$ (**l**)	92
		4-$C_6H_4NO_2$ (**m**)	94

[a]Conditions: aryl bromide (1.0 mmol), bis(pinacolato)diboron (1.2 mmol), 1 mol % **4a**, KOAc (2 mmol), *i*-PrOH (4 mL), 85 °C, 6 h. The isolated yields are an average of two independent runs. [b]After 24 h.

featuring the strongly electron-donating methoxy substituent. Other compounds reacted smoothly, affording the corresponding boronates in yields exceeding 85%. No biaryls were detected among the products of these reactions.

CONCLUSION

Although the synthetic approach presented in this contribution is based on time-tested methods, it provides an efficient and convenient access to a range of novel, structurally unique chelating phosphino-diaminocarbene ligands. In particular, the family of phosphinoferrocene imidazol-2-ylidenes was extended by their hitherto unknown saturated counterparts (imidazolin-2-ylidenes) and by their analogous open protic diaminocarbenes. However, even for phosphinoferrocene imidazol-2-ylidenes, the newly introduced, one-pot approach proved more efficient than the conventional convergent approach (synthesis of a heterocyclic precursor, deprotonation, and coordination). More importantly, compounds derived from phosphinoferrocene isocyanide **1** bear a carbene moiety directly bonded to the ferrocene core (i.e., without any inserted spacer, typical of previously reported compounds), which in turn increases the stereochemical rigidity and allows for electronic conjugation between the ferrocene unit and the carbene moiety.

Aminocarbene ligands (especially heterocyclic) are often matched against phosphines. This is perhaps inevitable, especially when considering the dominant role of the dppf ligand in coordination chemistry and catalysis.[35] In this particular case, the electrochemical data suggested that the reported phosphinoferrocene diaminocarbene ligands are more electron rich (hence, better donating) ligands than dppf, in agreement with general trends. When applied in Miyaura borylation of aryl bromines, some of the prepared Pd(II) complexes featuring P,C-chelating phosphinoferrocene carbene ligands outperformed the benchmark catalyst [$PdCl_2$(dppf)] in both activity and selectivity.

EXPERIMENTAL SECTION

Materials and Methods. The syntheses were performed under argon using standard Schlenk techniques and oven-dried glassware. Isocyanide **1**[17] and [$PdCl_2$(dppf)][36] were prepared by following the literature methods. The syntheses of *N*-(2,2-dimethoxyethyl)-2-propanamine, *N*-(2-chloroethyl)methylamine hydrochloride, and (*S*)-2-(chloromethyl)pyrrolidine hydrochloride are described in the

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Supporting Information. Other chemicals were purchased from commercial suppliers (Sigma-Aldrich or Alfa-Aesar) and were used as received. Anhydrous dichloromethane used for syntheses was obtained from an in-house PureSolv MD5 solvent purification system (Innovative Technology). Triethylamine and isopropanol utilized during catalytic tests were dried by adding some CaH_2 and by distillation. The solvents used for crystallizations and for chromatography (reagent grade from Lach-Ner) were utilized as received.

^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded with a Varian Unity Inova 400, a Bruker AVANCE 400 (^1H, 400 MHz; ^{31}P, 162 MHz; and ^{13}C, 101 MHz; ^{11}B, 128 MHz) or a Bruker AVANCE III 600 (^1H, 600 MHz; ^{13}C, 151 MHz) spectrometer at 25 °C. Chemical shifts (δ in ppm) are quoted relative to internal tetramethylsilane (^1H and ^{13}C), to external 85% aqueous H_3PO_4 (^{31}P), and to external $BF_3{\cdot}OEt_2$ (^{11}B). IR spectra in Nujol mulls were acquired with a Thermo Nicolet 6700 instrument over the 400−4000 cm^{-1} range. Electrospray ionization (ESI) mass spectra were recorded on a Compact QTOF-MS spectrometer (Bruker Daltonics). Electronic circular dichroism (ECD) spectra were collected on a Jasco 815 spectrometer over the spectral range 220−400 nm using a 0.01 cm cylindrical quartz cell at room temperature (experimental setup: 0.1 nm step, 20 nm min^{-1} scan range, 4 s response time, and 1 nm spectral bandwidth). The spectra were corrected on the baseline. The samples were dissolved in dichloromethane to 0.1 mM. Optical rotations were determined on an AUTOPOL IV automatic polarimeter (Rudolph Research Analytical). Elemental analyses were performed on a PE 2400 Series II CHNS/O elemental analyzer (PerkinElmer). The amount of clathrated solvent(s) was verified by NMR analysis.

Electrochemical measurements were performed using a μAUTOLAB III multipurpose potentiostat (Eco Chemie) at room temperature and using a three-electrode cell with a platinum disc electrode (2 mm diameter) as the working electrode, a platinum sheet auxiliary electrode, and a double-junction Ag/AgCl (3 M KCl) reference electrode. The analyzed compounds were dissolved in anhydrous dichloromethane to give a solution containing 1 mM of the analyte and 0.1 M $Bu_4N[PF_6]$ (Fluka, puriss. for electrochemistry) as the supporting electrolyte. The solutions were deaerated with argon before the measurements and then kept under an argon blanket. Decamethylferrocene (Alfa-Aesar) was added as an internal standard for the final scans, and the redox potentials were converted into the ferrocene/ferrocenium scale by subtracting 0.548 V.[37]

Syntheses. Synthesis of ***2a****.* A solution of isocyanide **1** (79 mg, 0.20 mmol) in dry dichloromethane (2 mL) was added to a stirring solution of $[PdCl_2(cod)]$ (57 mg, 0.20 mmol) in the same solvent (3 mL), immediately followed by a methylamine solution (0.12 mL of 2 M in THF, 0.25 mmol). The resulting mixture was stirred at room temperature overnight (a precipitate gradually separated during this time) and then evaporated under vacuum. The crude product was purified by column chromatography (silica gel, dichloromethane−methanol 20:1). The first, minor brown band was discarded, and the following, tailing orange band was collected and evaporated under vacuum to give **2a** as an orange solid. Yield: 62 mg (52%). The compound is a 2:1 mixture of isomers.

^1H NMR (CD_2Cl_2/CD_3OD, 400 MHz): δ, *major isomer*, 2.94 (s, 3 H, NMe), 4.26 (td, J' = 2.6 Hz, 1.3 Hz, 1 H, CH of fc), 4.38 (td, J' = 2.7 Hz, 1.5 Hz, 1 H, CH of fc), 4.59−4.61 (m, 2 H, 2× CH of fc), 4.75 (m, 1 H, CH of fc), 4.77 (td, J' = 2.7 Hz, 1.3 Hz, 1 H, CH of fc), 5.48 (td, J' = 2.7 Hz, 1.3 Hz, 1 H, CH of fc), 5.73 (dq, J' = 5.0 Hz, 1.3 Hz, 1 H, CH of fc), 7.35−7.56 (m, 6 H, PPh_2), 7.59−7.69 (m, 4 H, PPh_2); *minor isomer*, 2.30 (s, 3 H, NMe), 4.32 (td, J' = 2.6 Hz, 1.4 Hz, 1 H, CH of fc), 4.41 (td, J' = 2.7 Hz, 1.5 Hz, 1 H, CH of fc), 4.64 (td, J' = 2.6 Hz, 1.3 Hz, 1 H, CH of fc), 4.66 (td, J' = 2.5 Hz, 1.3 Hz, 1 H, CH of fc), 4.80 (m, 1 H, CH of fc), 4.82 (td, J' = 2.6 Hz, 1.2 Hz, 1 H, CH of fc), 5.57 (dt, J' = 2.6 Hz, 1.2 Hz, 1 H, CH of fc), 5.77 (dq, J' = 5.2 Hz, 1.3 Hz, 1 H, CH of fc), 7.35−7.56 (m, 6 H, PPh_2), 7.59−7.69 (m, 4 H, PPh_2). The signals of the NH protons were not observed due to H−D exchange. ^{13}C NMR spectra could not be obtained given the low solubility of the compound. $^{31}P\{^1H\}$ NMR (CD_2Cl_2/CD_3OD, 162 MHz): δ 17.75 (s, major isomer), 17.77 (s, minor isomer). MS ESI+: m/z 531 ($[M - HCl - Cl]^+$), 567 ($[M - Cl]^+$). IR (Nujol) ν_{max}/cm^{-1}: 3443 br w, 3197 br m, 3054 m, 1581 vs (carbene), 1252 w, 1200 w, 1169 m, 1099 s, 1050 w, 1030 s, 999 w, 934 m, 824 m, 746 s, 695 s, 628 m, 571 w, 526 s, 498 s, 480 s, 444 m. Anal. Calcd for $C_{24}H_{23}Cl_2FeN_2PPd{\cdot}0.1\ CHCl_3$ (615.5): C, 47.03%; H, 3.78%; N, 4.55%; Found: C, 47.03%; H, 3.96%; N, 4.26%.

Synthesis of ***2b****.* Compound **2b** was prepared analogously to **2a**, starting from isocyanide **1** (79 mg, 0.20 mmol), $[PdCl_2(cod)]$ (57 mg, 0.20 mmol), and neat isopropyl amine (26 μL, 0.30 mmol). Isolation as described above gave pure **2b** as an orange solid (single isomer). Yield: 81 mg (64%). Crystals used for structure determination were obtained from chloroform/hexane.

^1H NMR (CD_2Cl_2, 400 MHz): δ 0.39 (d, $^3J_{HH}$ = 6.5 Hz, 3 H, $CHMe_2$), 1.30 (d, $^3J_{HH}$ = 6.5 Hz, 3 H, $CHMe_2$), 4.14 (dt, J' = 2.6 Hz, 1.2 Hz, 1 H, CH of fc), 4.30 (dt, J' = 2.6 Hz, 1.2 Hz, 1 H, CH of fc), 4.38 (dt, J' = 2.6 Hz, 1.2 Hz, 1 H, CH of fc), 4.43 (td, J' = 2.5 Hz, 1.3 Hz, 1 H, CH of fc), 4.54 (br s, 1 H, CH of fc), 4.58 (m, 1 H, $CHMe_2$), 5.11 (br s, 1 H, CH of fc), 5.50 (br s, 1 H, CH of fc), 5.56 (br s, 1 H, CH of fc), 7.32−7.62 (m, 10 H, PPh_2), 8.12 (br d, $^3J_{HH}$ = 9.2 Hz, 1 H, *i*-PrN*H*), 8.86 (br s, 1 H, fcN*H*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 151 MHz): δ 21.74 ($CHMe_2$), 23.11 ($CHMe_2$), 54.62 (d, $^4J_{HH}$ = 3 Hz, $CHMe_2$), 63.30 (CH of fc), 66.12 (CH of fc), 66.20 (d, $^1J_{PC}$ = 63 Hz, C^{ipso}-P of fc), 68.52 (CH of fc), 68.73 (CH of fc), 71.90 (d, $^2J_{PC}$ = 6 Hz, CH of fc), 74.21 (d, $^3J_{PC}$ = 5 Hz, CH of fc), 74.57 (d, $^3J_{PC}$ = 10 Hz, CH of fc), 78.20 (d, $^2J_{PC}$ = 20 Hz, CH of fc), 104.15 (d, $^4J_{PC}$ = 3 Hz, C^{ipso}-N of fc), 128.28 (d, J_{PC} = 12 Hz, CH of PPh_2), 129.53 (d, J_{PC} = 11 Hz, CH of PPh_2), 129.63 (d, $^1J_{PC}$ = 55 Hz, C^{ipso}-P of PPh_2), 131.09 (d, $^1J_{PC}$ = 55 Hz, C^{ipso}-P of PPh_2), 131.11 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 131.28 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 133.21 (d, J_{PC} = 10 Hz, CH of PPh_2), 134.59 (d, J_{PC} = 12 Hz, CH of PPh_2), 193.45 (d, $^2J_{PC}$ = 6 Hz, carbene C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162 MHz): δ 17.8 (s). MS ESI+: m/z 559 ($[M - HCl - Cl]^+$), 596 ($[M - Cl]^+$). IR (Nujol) ν_{max}/cm^{-1}: 3187 br m, 3034 br m, 1570 s, 1527 m, 1293 w, 1247 w, 1169 s, 1099 m, 1029 m, 1000 w, 932 w, 821 m, 745 s, 695 s, 628 w, 536 w, 520 s, 479 s, 443 w. Anal. Calcd for $C_{26}H_{27}Cl_2FeN_2PPd$ (631.6): C, 49.44%; H, 4.31%; N, 4.44%. Found: C, 49.29%; H, 4.46%; N, 4.16%.

Synthesis of ***3a****.* To a stirring solution of $[PdCl_2(cod)]$ (57 mg, 0.20 mmol) in anhydrous dichloromethane (3 mL), the following reagents were added, in rapid succession: isocyanide **1** (79 mg, 0.20 mmol), dissolved in the same solvent (2 mL), and a solution of dimethylamine, prepared separately by mixing dimethylamine hydrochloride (24.5 mg, 0.30 mmol) and triethylamine (0.1 mL, 0.7 mmol) in dry dichloromethane (2 mL). The deep red mixture was stirred overnight and then washed with saturated aqueous NH_4Cl and evaporated under vacuum. The crude product was purified by column chromatography (silica gel, dichloromethane−methanol 10:1). The first minor band containing some impurities was discarded, and the following major orange−brown band due to the product was collected and evaporated. The resulting solid was redissolved in chloroform (2 mL) and crystallized by layering with hexane (10 mL). The orange crystals of **3a**, which separated during several days, were isolated by suction and dried under vacuum. Yield: 43 mg (35%). Crystals used for structure determination were obtained from chloroform/hexane.

^1H NMR (CD_2Cl_2/CD_3OD, 400 MHz): δ 2.47 (s, 3 H, NMe), 3.41 (s, 3 H, NMe), 4.32 (td, J' = 2.6 Hz, 1.4 Hz, 1 H, CH of fc), 4.42 (td, J' = 2.6 Hz, 1.5 Hz, 1 H, CH of fc), 4.63 (td, J' = 2.6 Hz, 1.4 Hz, 1 H, CH of fc), 4.66 (dq, J' = 2.6 Hz, 1.4 Hz, 1 H, CH of fc), 4.82 (m, 1 H CH of fc), 4.87 (dt, J' = 2.6 Hz, 1.5 Hz, 1 H, CH of fc), 5.69 (dt, J' = 2.7 Hz, 1.4 Hz, 1 H, CH of fc), 5.86 (dq, J' = 2.6 Hz, 1.3 Hz, 1 H, CH of fc), 7.38−7.44 (m, 5 H, PPh_2), 7.46−7.51 (m, 1 H, PPh_2), 7.54−7.60 (m, 2 H, PPh_2), 7.65−7.71 (m, 2 H, PPh_2). The signals of the NH protons were not observed due to H−D exchange. $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CD_3OD, 151 MHz): δ 38.49 (NMe), 48.09 (d, $^4J_{PC}$ = 3 Hz, NMe), 64.04 (CH of fc), 65.80 (d, $^1J_{PC}$ = 62 Hz, C^{ipso}-P of fc), 66.51 (CH of fc), 68.57 (CH of fc), 68.73 (CH of fc), 72.89 (d, $^2J_{PC}$ = 6 Hz, CH of fc), 74.62 (d, $^3J_{PC}$ = 4 Hz, CH of fc), 74.83 (d, $^3J_{PC}$ = 11 Hz, CH of fc), 79.07 (d, $^2J_{PC}$ = 21 Hz, CH of fc), 103.65 (d, $^4J_{PC}$ = 3 Hz, C^{ipso}-N of fc), 128.39 (d, J_{PC} = 12 Hz, CH of PPh_2), 128.91 (d,

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J_{PC} = 11 Hz, CH of PPh_2), 130.76 (d, $^1J_{PC}$ = 54 Hz, C^{ipso} of PPh_2), 131.09 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 131.22 (d, $^1J_{PC}$ = 56 Hz, C^{ipso} of PPh_2), 131.60 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 132.05 (d, J_{PC} = 10 Hz, CH of PPh_2), 134.69 (d, J_{PC} = 12 Hz, CH of PPh_2), 194.55 (d, $^2J_{PC}$ = 7 Hz, carbene C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2/CD_3OD, 162 MHz): δ 17.9 (s). MS ESI+: m/z 475 ([M − PdCl]$^+$), 545 ([M − HCl − Cl]$^+$). IR (Nujol) ν_{max}/cm^{-1}: 3454 br w, 3212 br m, 3053 m, 1572 vs (carbene), 1342 m, 1310 w, 1267 m, 1219 w, 1167 s, 1099 s, 1029 s, 999 w, 948 w, 889 m, 821 m, 749 s, 694 s, 663 w, 629 w, 537 m, 526 s, 518 s, 498 s, 479 s, 443 w. Anal. Calcd for $C_{25}H_{25}Cl_2FeN_2PPd{\cdot}0.2\ CHCl_3$ (641.4): C, 47.18%; H, 3.96%; N, 4.37%. Found: C, 47.05%; H, 4.36%; N, 4.31%.

Synthesis of ***3b***. Diisopropylamine (34 μL, 0.25 mmol) and isocyanide **1** (79 mg, 0.20 mmol in 4 mL of dichloromethane) were successively added to a solution of [$PdCl_2$(cod)] (57 mg, 0.20 mmol) in dichloromethane (2 mL). The mixture was stirred at room temperature overnight and evaporated under vacuum. The residue was purified by chromatography (silica gel, dichloromethane−methanol 20:1). Evaporation of the second band afforded **3b** as an orange−red solid. Yield: 73 mg (54%). Single crystals used for structure determination were formed upon layering a solution of the compound in chloroform−ethyl acetate with hexane.

^1H NMR (CD_2Cl_2/CD_3OD, 400 MHz): δ 0.50 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, CHMe_2), 1.08 (d, $^3J_{HH}$ = 7.4 Hz, 3 H, CHMe_2), 1.32 (d, $^3J_{HH}$ = 7.3 Hz, 3 H, CHMe_2), 1.41 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, CHMe_2), 3.62 (septet, $^3J_{HH}$ = 7.3 Hz, 1 H, CHMe$_2$), 4.36 (td, J_{HH} = 2.6 Hz, 1.3 Hz, 1 H, CH of fc), 4.39 (dq, J_{HH} = 2.7 Hz, 1.3 Hz, 1 H, CH of fc), 4.47 (td, J_{HH} = 2.7 Hz, 1.5 Hz, 1 H, CH of fc), 4.61 (td, J_{HH} = 2.6 Hz, 1.4 Hz, 1 H, CH of fc), 4.70 (dt, J_{HH} = 2.6 Hz, 1.4 Hz, 1 H, CH of fc), 4.83 (m, 1 H, CH of fc), 5.75 (dt, J_{HH} = 2.7 Hz, 1.3 Hz, 1 H, CH of fc), 5.82 (br sept, $^3J_{HH} \approx$ 6.7 Hz, 1 H, CHMe$_2$), 5.90 (dq, $^3J_{PH}$ = 4.7 Hz, $^3J_{HH}$ = 1.3 Hz, 1 H, CH of fc), 7.33−7.39 (m, 2 H, PPh_2), 7.41−7.53 (m, 6 H, PPh_2), 7.59−7.65 (m, 2 H, PPh_2). The NH signals were not observed due to H−D exchange. $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CD_3OD, 151 MHz): δ 19.20 (CHMe_2), 19.65 (CHMe_2), 20.07 (CHMe_2), 21.63 (CHMe_2), 47.84 (CHMe$_2$), 64.01 (d, $^4J_{PC}$ = 4 Hz, CHMe$_2$), 64.48 (CH of fc), 66.15 (d, $^1J_{PC}$ = 61 Hz, C^{ipso}-P of fc), 66.45 (CH of fc), 68.43 (CH of fc), 68.87 (CH of fc), 72.82 (d, $^3J_{PC}$ = 6 Hz, CH of fc), 74.14 (d, $^3J_{PC}$ = 5 Hz, CH of fc), 75.19 (d, $^2J_{PC}$ = 11 Hz, CH of fc), 79.09 (d, $^2J_{PC}$ = 20 Hz, CH of fc), 103.75 (d, $^4J_{PC}$ = 3 Hz, C^{ipso}-N of fc), 128.29 (d, J_{PC} = 12 Hz, CH of PPh_2), 129.22 (d, J_{PC} = 11 Hz, CH of PPh_2), 131.03 (d, $^1J_{PC}$ = 55 Hz, C^{ipso} of PPh_2), 131.05 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 131.35 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 131.38 (d, $^1J_{PC}$ = 53 Hz, C^{ipso} of PPh_2), 132.98 (d, J_{PC} = 9 Hz, CH of PPh_2), 134.52 (d, J_{PC} = 12 Hz, CH of PPh_2), 193.19 (d, $^2J_{PC}$ = 8 Hz, carbene C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2/CD_3OD, 162 MHz): δ 16.3 (s). IR (Nujol) ν_{max}/cm^{-1}: 3438 br m, 3413 m, 3335 br m, 3130 w, 3092 m, 3078 m, 3052 m, 1546 vs (carbene), 1320 s, 1218 w, 1204 w, 1188 m, 1168 m, 1141 m, 1105 m, 1093 m, 1059 w, 1048 w, 1036 m, 1019 w, 1000 w, 941 w, 907 w, 838 s, 749 s, 702 m, 694 s, 649 m, 636 m, 539 m, 525 m, 498 m, 483 s, 469 m, 441 m. MS ESI+: m/z 601 ([M − HCl − Cl]$^+$). Anal. Calcd for $C_{29}H_{33}N_2Cl_2FePPd{\cdot}0.66\ CH_2Cl_2$ (729.8): C, 48.81%; H, 4.74%; N, 3.84%. Found C, 48.72%; H, 4.74%; N, 3.47%.

Synthesis of ***4a***. Anhydrous triethylamine (0.20 mL, 1.4 mmol) was added to a suspension of *N*-(2-chloroethyl)methylamine hydrochloride (39 mg, 0.30 mmol) in dry dichloromethane (3 mL), causing the solid educt to rapidly dissolve. Next, solid [$PdCl_2$(cod)] (57 mg, 0.20 mmol) and a dichloromethane solution of **1** (79 mg, 0.20 mmol in 3 mL) were introduced in rapid succession. The resulting mixture was stirred overnight and then evaporated, leaving a residue, which was purified by column chromatography (silica gel, dichloromethane−methanol 20:1). The major orange band containing the product was collected and evaporated, affording compound **4a** as an orange glassy solid. Evaporation with chloroform gave a microcrystalline solid. Yield: 107 mg (85%). Crystals used for structure determination were grown by recrystallization from chloroform/methanol.

^1H NMR (CD_2Cl_2/CD_3OD, 400 MHz): δ 2.81 (ddd, $^3J_{HH}$ = 12.2 Hz, 10.3 Hz, $^2J_{HH}$ = 8.7 Hz, 1 H, MeNCH_2), 3.05 (s, 3 H, NMe), 3.49 (dddd, $^4J_{HH}$ = 1.7 Hz, $^3J_{HH}$ = 11.7 and 10.3 Hz, $^2J_{HH}$ = 8.7 Hz, 1 H, MeNCH_2), 3.72−3.86 (m, 2 H, fcNCH_2), 4.39 (td, J_{HH} = 2.7 Hz, 1.4 Hz, 1 H, CH of fc), 4.46 (td, J_{HH} = 2.7 Hz, 1.3 Hz, 1 H, CH of fc), 4.72 (td, J_{HH} = 2.6 Hz, 1.4 Hz, 1 H, CH of fc), 4.80−4.84 (m, 2 H, CH of fc), 4.87 (dt, J_{HH} = 2.6 Hz, 1.4 Hz, 1 H, CH of fc), 5.59 (dt, J_{HH} = 2.7 Hz, 1.4 Hz, 1 H, CH of fc), 5.90 (m, 1 H, CH of fc), 7.37−7.43 (m, 2 H, PPh_2), 7.45−7.50 (m, 4 H, PPh_2), 7.65−7.74 (m, 4 H, PPh_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CD_3OD, 151 MHz): δ 37.81 (NMe), 51.43 (MeNCH_2), 53.36 (fcNCH_2), 64.79 (CH of fc), 66.56 (d, $^1J_{PC}$ = 63 Hz, C^{ipso}-P of fc), 67.21 (CH of fc), 67.86 (CH of fc), 68.63 (CH of fc), 73.25 (d, $^3J_{PC}$ = 6 Hz, CH of fc), 74.57 (d, $^2J_{PC}$ = 11 Hz, CH of fc), 74.64 (d, $^3J_{PC}$ = 4 Hz, CH of fc), 79.42 (d, $^2J_{PC}$ = 22 Hz, CH of fc), 102.26 (d, $^4J_{PC}$ = 2 Hz, C^{ipso}-N of fc), 128.46 (d, J_{PC} = 12 Hz, CH of PPh_2), 129.13 (d, J_{PC} = 11 Hz, CH of PPh_2), 130.56 (d, $^1J_{PC}$ = 55 Hz, C^{ipso} of PPh_2), 131.37 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 131.61 (d, J_{PC} = 10 Hz, CH of PPh_2), 131.73 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 132.20 (d, $^1J_{PC}$ = 57 Hz, C^{ipso} of PPh_2), 134.64 (d, J_{PC} = 11 Hz, CH of PPh_2), 194.68 (d, $^2J_{PC}$ = 2 Hz, carbene C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2/CD_3OD, 162 MHz): δ 18.4 (s). IR (Nujol) ν_{max}/cm^{-1}: 3091 w, 3069 w, 1541 s (carbene), 1497 s (carbene), 1315 m, 1274 s, 1171 w, 1124 w, 1101 m, 1095 m, 1021 w, 936 w, 821 m, 761 m, 747 m, 733 m, 700 s, 652 w, 628 w, 616 m, 541 m, 528 s, 508 s, 483 s, 465 w, 443 w. MS ESI+: m/z 557 ([M − HCl − Cl]$^+$), 593 ([M − Cl]$^+$). Anal. Calcd for $C_{26}H_{25}Cl_2FeN_2PPd$ (629.6): C, 49.60%; H, 4.00%; N, 4.45%. Found: C, 49.71%; H, 3.98%; N, 4.27%.

Synthesis of ***5a***. Neat (methylamino)acetaldehyde dimethylacetal (26 μL, 0.20 mmol) was added to a suspension of [$PdCl_2$(cod)] (57 mg, 0.20 mmol) in dichloromethane (4 mL), thereby dissolving the solid educt and changing the color from yellow to orange. Next, a solution of **1** (79 mg, 0.20 mmol) in dichloromethane (4 mL) was introduced, and the red mixture was stirred at room temperature for 18 h. The crude product obtained by evaporation of the mixture was purified by column chromatography (silica gel, dichloromethane−methanol 10:1). The second, major red band was collected and evaporated, leaving **5a** as a red glassy solid. Yield: 121 mg, 85%. The compound is a mixture of isomers in a ratio of approximately 2:1.

^1H NMR (CD_2Cl_2/CD_3OD, 400 MHz): δ, *major isomer*, 2.60 (d, J = 0.4 Hz, 3 H, NMe), 3.14 (dd, J = 13.7 Hz, 7.8 Hz, 1 H, NCH_2), 3.37 (s, 3 H, OMe), 3.52 (s, 3 H, OMe), 4.35 (td, J_{HH} = 2.6 Hz, 1.3 Hz, 1 H, CH of fc), 4.44 (td, J_{HH} = 2.7 Hz, 1.5 Hz, 1 H, CH of fc), 4.60 (m, 1 H, CH of fc), 4.62 (dd, J_{HH} = 3.4 Hz, 1.1 Hz, 1 H, NCH_2), 4.64 (td, J_{HH} = 2.5 Hz, 1.1 Hz, 1 H, CH of fc), 4.83 (m, 1 H, CH of fc), 4.87 (dd, J_{HH} = 7.4 Hz, 3.4 Hz, CH(OMe)$_2$), 4.93 (dt, J_{HH} = 2.7 Hz, 1.3 Hz, 1 H, CH of fc), 5.87 (m, 1 H, CH of fc), 7.38−7.68 (m, 10 H, PPh_2); *minor isomer*, 2.87 (dd, J_{HH} = 15.1 Hz, 4.2 Hz, 1 H, NCH_2), 3.18 (t, J_{HH} = 3.9 Hz, 1 H, NCH_2), 3.37 (s, 6 H, OMe), 3.55 (s, 3 H, NMe), 4.17 (t, $^3J_{HH}$ = 4.6 Hz, 1 H, CH(OMe)$_2$), 4.36 (td, J_{HH} = 2.6 Hz, 1.3 Hz, 1 H, CH of fc), 4.45 (td, J_{HH} = 2.7 Hz, 1.5 Hz, 1 H, CH of fc), 4.60 (m, 1 H, CH of fc), 4.66 (m, 1 H, CH of fc), 4.71 (dt, J_{HH} = 2.8 Hz, 1.5 Hz, 1 H, CH of fc), 4.84 (m, 1 H, CH of fc), 5.66 (dt, J_{HH} = 2.7 Hz, 1.4 Hz, 1 H, CH of fc), 5.86 (m, 1 H, CH of fc), 7.38−7.68 (m, 10 H, PPh_2). Signals of the NH protons were not observed due to H−D exchange. $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CD_3OD, 151 MHz): δ *major isomer*, 38.55 (NMe), 56.02 (OMe), 56.30 (OMe), 62.56 (d, $^4J_{PC}$ = 3 Hz, NCH_2), 64.43 (CH of fc), 65.77 (d, $^1J_{PC}$ = 63 Hz, C^{ipso}-P of fc), 66.64 (CH of fc), 68.73 (CH of fc), 68.81 (CH of fc), 72.95 (d, $^3J_{PC}$ = 7 Hz, CH of fc), 74.61 (d, $^3J_{PC}$ = 5 Hz, CH of fc), 74.90 (d, $^2J_{PC}$ = 11 Hz, CH of fc), 79.00 (d, $^2J_{PC}$ = 21 Hz, CH of fc), 103.68 (d, $^4J_{PC}$ = 3 Hz, C^{ipso}-N of fc), 104.53 (CH(OMe)$_2$), 128.47 (d, J_{PC} = 11 Hz, CH of PPh_2), 129.12 (d, J_{PC} = 10 Hz, CH of PPh_2), 130.65 (d, $^1J_{PC}$ =55 Hz, C^{ipso} of PPh_2), 130.95 (d, $^1J_{PC}$ = 55 Hz, C^{ipso} of PPh_2), 131.22 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 131.66 (d, $^4J_{PC}$ = 2 Hz, CH^{para} of PPh_2), 132.21 (d, J_{PC} = 10 Hz, CH of PPh_2), 134.62 (d, J_{PC} = 11 Hz, CH of PPh_2), 196.25 (d, $^2J_{PC}$ = 7 Hz, carbene C); *minor isomer*, 47.94 (NMe), 55.97 (NCH_2), 56.19 (OMe), 56.66 (OMe), 64.72 (CH of fc), 65.70 (d, $^1J_{PC}$ = 63 Hz, C^{ipso}-P of fc), 66.75 (CH of fc), 68.83 (CH of fc), 68.86 (CH of fc), 73.06 (d, $^3J_{PC}$ = 4 Hz, CH of fc), 74.60 (d, $^3J_{PC}$ = 4 Hz, CH of fc), 74.98 (d, $^2J_{PC}$ = 11 Hz, CH of fc), 79.08 (d, $^2J_{PC}$ = 21 Hz, CH of fc), 103.24 (d, $^4J_{PC}$ = 2 Hz, C^{ipso}-N of fc), 103.49 (CH(OMe)$_2$), 128.42

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(d, J_{PC} = 11 Hz, CH of PPh_2), 128.99 (d, J_{PC} = 11 Hz, CH of PPh_2), 131.06 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 131.14 (d, $^1J_{PC}$ = 55 Hz, C^{ipso} of PPh_2), 131.16 (d, $^1J_{PC}$ = 55 Hz, C^{ipso} of PPh_2), 131.54 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 132.25 (d, J_{PC} = 10 Hz, CH of PPh_2), 134.47 (d, J_{PC} = 11 Hz, CH of PPh_2), 198.43 (d, $^2J_{PC}$ = 7 Hz, carbene C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2/CD_3OD, 162 MHz): δ 18.0 (s, major isomer), 17.2 (s, minor isomer). IR (Nujol) ν_{max}/cm^{-1}: 3445 br w, 3176 br m, 1560 vs (carbene), 1307 m, 1275 m, 1214 w, 1188 m, 1170 m, 1123 m, 1101 s, 1071 s, 1031 s, 999 w, 973 m, 900 m, 824 m, 750 s, 695 s, 630 w, 538 m, 525 m, 498 m, 481 s, 442 w. MS ESI+: m/z 619 ($[M - HCl - Cl]^+$), 657 ($[M - Cl]^+$). Anal. Calcd for $C_{28}H_{31}Cl_2FeN_2O_2PPd$ (691.7): C, 48.62%; H, 4.52%; N, 4.05. Found: C, 48.30%; H, 4.49%; N, 3.97%.

Compound ***5b***. Compound **5b** was prepared similarly to **5a**, using $[PdCl_2(cod)]$ (57 mg, 0.20 mmol), *N*-(2,2-dimethoxyethyl)-2-propanamine (44 mg, 0.30 mmol), and **1** (79 mg, 0.20 mmol). The crude product was purified by chromatography (silica gel, dichloromethane−methanol 20:1) and isolated as an orange−brown glassy solid (105 mg, 73%). Single crystals were grown from dichloromethane/hexane.

^1H NMR (CD_2Cl_2/CD_3OD, 400 MHz): δ 0.45 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, $CHMe_2$), 1.40 (d, $^3J_{HH}$ = 6.6 Hz, 3 H, $CHMe_2$), 3.21 (dd, J_{HH} = 15.8 Hz, 4.0 Hz, 1 H, NCH_2), 3.29 (dd, J_{HH} = 15.8 Hz, 4.6 Hz, 1 H, NCH_2), 3.38 (s, 3 H, OMe), 3.48 (s, 3 H, OMe), 4.10 (t, J_{HH} = 4.3 Hz, 1 H, $CH(OMe)_2$), 4.37 (m, 2 H, CH of fc), 4.47 (td, J_{HH} = 2.7 Hz, 1.4 Hz, 1 H, CH of fc), 4.62 (td, J_{HH} = 2.6 Hz, 1.3 Hz, 1 H, CH of fc), 4.65 (dt, J_{HH} = 2.6 Hz, 1.5 Hz, 1 H, CH of fc), 4.85 (m, 1 H, CH of fc), 5.71 (septet, $^3J_{HH}$ = 6.7 Hz, 1 H, $CHMe_2$), 5.74 (dt, J_{HH} = 2.7 Hz, 1.4 Hz, 1 H, CH of fc), 5.82 (ddd, $^3J_{PH}$ = 3.4 Hz, J_{HH} = 2.6 Hz, 1.3 Hz, 1 H, CH of fc), 7.38−7.47 (m, 7 H, PPh_2), 7.51−7.54 (m, 1 H, PPh_2), 7.57−7.64 (m, 2 H, PPh_2). The signals due to NH protons were not observed. $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CD_3OD, 151 MHz): δ 20.20 ($CHMe_2$), 20.22 ($CHMe_2$), 49.81 (s, NCH_2), 54.87 (OMe), 55.78 (OMe), 62.21 (d, $^4J_{PC}$ = 4 Hz, $CHMe_2$), 64.62 (CH of fc), 66.51 (d, $^1J_{PC}$ = 62 Hz, C^{ipso}-P of fc), 66.79 (CH of fc), 68.03 (CH of fc), 69.00 (CH of fc), 72.82 (d, $^3J_{PC}$ = 7 Hz, CH of fc), 74.53 (d, $^3J_{PC}$ = 5 Hz, CH of fc), 75.26 (d, $^2J_{PC}$ = 11 Hz, CH of fc), 78.73 (d, $^2J_{PC}$ = 20 Hz, CH of fc), 103.62 (d, $^4J_{PC}$ = 3 Hz, C^{ipso}-N of fc), 104.71 ($CH(OMe)_2$), 128.47 (d, J_{PC} = 12 Hz, CH of PPh_2), 129.15 (d, J_{PC} = 10 Hz, CH of PPh_2), 130.78 (d, $^1J_{PC}$ = 56 Hz, C^{ipso} of PPh_2), 131.37 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 131.37 (d, $^1J_{PC}$ = 54 Hz, C^{ipso} of PPh_2), 131.60 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 133.09 (d, J_{PC} = 10 Hz, CH of PPh_2), 134.63 (d, J_{PC} = 11 Hz, CH of PPh_2), 197.49 (d, $^2J_{PC}$ = 8 Hz, carbene C). IR (Nujol) ν_{max}/cm^{-1}: 3197 br m, 1714 m, 1547 s (carbene), 1304 w, 1219 w, 1169 w, 1123 m, 1095 m, 1072 m, 1032 m, 971 w, 915 w, 817 m, 748 m, 697 s, 678 w, 630 w, 536 m, 525 s, 486 s, 474 s, 444 w. MS ESI+: m/z 647 ($[M - HCl - Cl]^+$), 683 ($[M - Cl]^+$). Anal. Calcd for $C_{30}H_{35}Cl_2FeN_2O_2PPd \cdot 0.66CH_2Cl_2$ (775.8): C, 47.47%; H, 4.72%; N, 3.61%. Found: C, 47.21%; H, 4.62%; N, 3.55%.

Synthesis of ***6a***. Complex **5a** (102 mg, 0.15 mmol) was dissolved in dry dichloromethane (10 mL), and the solution was treated with HCl (1 mL of 4 M solution in dioxane, 0.25 mmol). After stirring overnight, the reaction mixture was evaporated, and the residue was purified by chromatography (silica gel, dichloromethane−methanol 50:1). A single rusty brown band was collected and evaporated, producing **6a** as a rusty brown glassy solid (91 mg, 97%). Crystals suitable for X-ray diffraction analysis were grown from dichloromethane/hexane.

^1H NMR (CD_2Cl_2/CD_3OD, 400 MHz): δ 3.45 (s, 3 H, NMe), 4.49 (td, J = 2.7 Hz, 1.4 Hz, 1 H, CH of fc), 4.60 (td, J = 2.7 Hz, 1.4 Hz, 1 H, CH of fc), 4.65 (dt, J = 2.7 Hz, 1.3 Hz, 1 H, CH of fc), 4.76 (td, J = 2.6 Hz, 1.3 Hz, 1 H, CH of fc), 4.88 (m, 1 H, CH of fc), 4.97 (dt, J = 2.7 Hz, 1.4 Hz, 1 H, CH of fc), 5.78 (dt, J = 2.7 Hz, 1.3 Hz, 1 H, CH of fc), 5.93 (m, 1 H, CH of fc), 6.67 (d, $^3J_{HH}$ = 2.0 Hz, CH of imidazole), 7.08−7.13 (m, 2 H, PPh_2), 7.10 (d, $^3J_{HH}$ = 2.0 Hz, CH of imidazole), 7.18−7.24 (m, 2 H, PPh_2), 7.28−7.34 (m, 1 H, PPh_2), 7.38−7.43 (m, 2 H, PPh_2), 7.46−7.51 (m, 1 H, PPh_2), 7.64−7.77 (m, 2 H, PPh_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CD_3OD, 151 MHz): δ 38.11 (NMe), 66.55 (CH of fc), 67.23 (CH of fc), 67.77 (d, $^1J_{PC}$ = 62 Hz, C^{ipso}-P of fc), 67.84 (CH of fc), 69.85 (CH of fc), 73.36 (d, $^3J_{PC}$ = 6 Hz, CH of fc), 74.18 (d, $^2J_{PC}$ = 3 Hz, CH of fc), 74.87 (d, $^3J_{PC}$ = 11 Hz, CH of fc), 73.32 (d, $^2J_{PC}$ = 22 Hz, CH of fc), 100.83 (d, $^4J_{PC}$ = 2 Hz, C^{ipso}-N of fc), 124.35 (CH of imidazole), 124.66 (CH of imidazole), 128.30 (d, J_{PC} = 12 Hz, CH of PPh_2), 129.22 (d, J_{PC} = 10 Hz, CH of PPh_2), 130.05 (d, $^1J_{PC}$ = 56 Hz, C^{ipso} of PPh_2), 130.31 (d, J_{PC} = 10 Hz, CH of PPh_2), 130.57 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 131.60 (d, $^1J_{PC}$ = 58 Hz, C^{ipso} of PPh_2), 131.63 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 134.69 (d, J_{PC} = 11 Hz, CH of PPh_2), 164.76 (carbene C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2/CD_3OD, 162 MHz): δ 17.2 (s). IR (Nujol) ν_{max}/cm^{-1}: 3160 w, 3086 m, 1571 m, 1497 s, 1307 s, 1296 m, 1246 m, 1202 w, 1171 m, 1141 w, 1126 m, 1097 s, 1042 s, 1034 s, 999 m, 974 w, 880 w, 840 s, 747 s, 702 s, 695 s, 684 s, 628 w, 542 m, 518 s, 509 s, 481 s, 446 m. MS ESI+: m/z 555 ($[M - HCl - Cl]^+$), 590 ($[M - Cl]^+$). Anal. Calcd for $C_{26}H_{23}Cl_2FeN_2PPd \cdot CH_2Cl_2$ (712.5): C, 45.51%; H, 3.54%; N, 3.93%. Found: C, 45.45%; H, 3.40%; N, 3.77%.

Synthesis of ***6b***. Compound **6b** was prepared similarly from **5b** (105 mg, 0.15 mmol) and isolated as an orange brown glassy solid. Yield: 89 mg (93%). The compound was crystallized from dichloromethane/hexane.

^1H NMR (CD_2Cl_2/CD_3OD, 400 MHz): δ 0.52 (d, $^3J_{HH}$ = 6.8 Hz, 3 H, $CHMe_2$), 1.44 (d, $^3J_{HH}$ = 6.7 Hz, 3 H, $CHMe_2$), 4.44 (dt, J_{HH} = 2.7 Hz, 1.3 Hz, 1 H, CH of fc), 4.49 (td, J_{HH} = 2.7 Hz, 1.4 Hz, 1 H, CH of fc), 4.61 (td, J_{HH} = 2.7 Hz, 1.4 Hz, 1 H, CH of fc), 4.71 (td, J_{HH} = 2.6 Hz, 1.4 Hz, 1 H, CH of fc), 4.89 (dt, J_{HH} = 2.6 Hz, 1.4 Hz, 1 H, CH of fc), 4.97 (dt, J_{HH} = 2.7 Hz, 1.4 Hz, 1 H, CH of fc), 5.11 (sept, $^3J_{HH}$ = 6.8 Hz, 1 H, $CHMe_2$), 5.83 (dt, J_{HH} = 2.8 Hz, 1.4 Hz, 1 H, CH of fc), 5.91 (m, 1 H, CH of fc), 6.85−6.90 (m, 2 H, PPh_2), 6.88 (d, $^3J_{HH}$ = 2.1 Hz, 1 H, CH of imidazole), 7.15−7.22 (m, 2 H, PPh_2), 7.23 (dd, $^3J_{HH}$ = 2.1 Hz, J = 0.4 Hz, 1 H, CH of imidazole), 7.29−7.34 (m, 1 H, PPh_2), 7.40−7.46 (m, 2 H, PPh_2), 7.48−7.53 (m, 1 H, PPh_2), 7.56−7.63 (m, 2 H, PPh_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2/CD_3OD, 151 MHz): δ 21.43 ($CHMe_2$), 23.31 ($CHMe_2$), 54.38 ($CHMe_2$), 66.65 (CH of fc), 67.22 (CH of fc), 67.79 (CH of fc), 68.58 (d, $^1J_{HH}$ = 62 Hz, C^{ipso}-P of fc), 69.87 (CH of fc), 73.02 (d, $^3J_{PC}$ = 6 Hz, CH of fc), 74.12 (d, $^2J_{PC}$ = 4 Hz, CH of fc), 75.10 (d, $^3J_{PC}$ = 11 Hz, CH of fc), 78.99 (d, $^2J_{PC}$ = 21 Hz, CH of fc), 101.27 (d, J_{PC} = 2 Hz, C^{ipso}-N of fc), 119.33 (CH of imidazole), 125.53 (CH of imidazole), 128.33 (d, $^2J_{PC}$ = 12 Hz, CH^{ortho} of PPh_2), 129.36 (d, $^3J_{PC}$ = 10 Hz, CH^{meta} of PPh_2), 129.91 (d, $^1J_{PC}$ = 56 Hz, C^{ipso} of PPh_2), 130.98 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 131.23 (d, $^1J_{PC}$ = 56 Hz, C^{ipso} of PPh_2), 131.29 (d, $^3J_{PC}$ = 9 Hz, CH^{meta} of PPh_2), 131.65 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of Ph), 134.71 (d, $^2J_{PC}$ = 11 Hz, CH^{ortho} of PPh_2), 162.68 (carbene C). $^{31}P\{^1H\}$ NMR (CD_2Cl_2/CD_3OD, 162 MHz): δ 18.1 (s). MS ESI+: m/z 583 ($[M - HCl - Cl]^+$), 619 ($[M - Cl]^+$), 679 ($[M + Na]^+$). IR (Nujol) ν_{max}/cm^{-1}: 3160 w, 3122 m, 3096 m, 3065 w, 1636 m, 1572 m, 1492 s (carbene), 1482 s (carbene), 1418 m, 1311 m, 1287 m, 1231 m, 1247 w, 1171 m, 1131 m, 1099 m, 1073 w, 1061 w, 1044 w, 1031 m, 1000 w, 957 w, 888 w, 871 m, 847 w, 829 m, 821 m, 744 s, 708 s, 691 s, 658 w, 643 w, 629 m, 560 w, 541 m, 531 m, 512 s, 482 s, 462 w, 445 m. Anal. Calcd for $C_{28}H_{27}Cl_2FeN_2PPd$ (656.0): C, 51.29%; H, 4.15%; N, 4.27%. Found: C, 50.91%; H, 3.99%; N, 4.19%.

Compound ***7***. (*S*)-2-(Chloromethyl)pyrrolidine hydrochloride (49 mg, 0.30 mmol) was dissolved in dry dichloromethane (3 mL). To this solution, the following reagents were successively added: anhydrous triethylamine (0.10 mL, 0.7 mmol), $[PdCl_2(cod)]$ (57 mg, 0.20 mmol), and a dichloromethane solution of isocyanide **1** (79 mg, 0.20 mmol in 2 mL). The orange reaction mixture was stirred overnight and then evaporated under vacuum. The crude product was purified by chromatography over a silica gel column with dichloromethane−methanol 20:1, yielding the product as a 3:2 mixture of diastereoisomers (83 mg, 63%; see Chart 4). The diastereoisomers were separated by chromatography over silica gel (dichloromethane−methanol 50:1) and subsequent chromatographic purification on a Sepacore Flash System X50 (Büchi) using gradient elution with a similar solvent mixture. Yield of (S,R_p)-**7**: orange solid; 46 mg (35%). Single crystals were obtained from chloroform/hexane. Yield of (S,S_p)-**7**: orange solid; 31 mg (24%).

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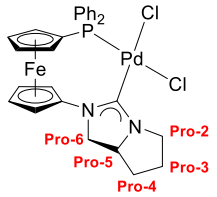
Chart 4. Labeling Scheme of Proline Carbene 7



Analytical data for (S,R_p)-7. $[\alpha]^{20}_{589}$ = −295 (c = 0.33, CH_2Cl_2). ^{1}H NMR (CD_2Cl_2, 600 MHz): δ 1.39 (tdt, J_{HH} = 11.8 Hz, 10.3 Hz, 9.0 Hz, 1 H, Pro-4), 1.68 (m, 1 H, Pro-3), 1.83 (m, 1 H, Pro-4), 2.09 (dtdd, J_{HH} = 13.3 Hz, 8.9 Hz, 4.5 Hz, 2.0 Hz, 1 H, Pro-3), 2.97 (m, 1 H, Pro-6), 3.30 (tt, J_{HH} = 10.5 Hz, 6.5 Hz, 1 H, Pro-5), 3.50 (dd, $^2J_{HH}$ = 10.4 Hz, $^3J_{HH\text{-}syn}$ = 6.9 Hz, 1 H, Pro-6), 3.76 (t, $^3J_{HH\text{-}anti} \approx {}^2J_{HH}$ = 10.4 Hz, 1 H, Pro-6), 4.35 (td, J = 2.7 Hz, 1.4 Hz, 1 H, CH of fc), 4.43 (td, J = 2.7 Hz, 1.4 Hz, 1 H, CH of fc), 4.53 (ddd, J_{HH} = 11.2 Hz, 8.7 Hz, 6.8 Hz, 1 H, Pro-2), 4.66 (td, J = 2.6 Hz, 1.3 Hz, 1 H, CH of fc), 4.78 (tdd, J = 2.6 Hz, 1.7 Hz, 1.2 Hz, 1 H, CH of fc), 4.79 (dt, J = 2.6 Hz, 1.7 Hz, 1.2 Hz, 1 H, CH of fc), 4.80 (dt, J = 2.7 Hz, 1.4 Hz, 1 H CH of fc), 5.70 (dt, J = 2.8 Hz, 1.4 Hz, 1 H, CH of fc), 5.98 (ddt, J = 3.9 Hz, 2.6 Hz, 1.3 Hz, 1 H, CH of fc), 7.35−7.39 (m, 2 H, PPh_2), 7.40−7.46 (m, 4 H, PPh_2), 7.66−7.73 (m, 4 H, PPh_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 151 MHz): δ 24.59 (Pro-3), 30.89 (Pro-4), 46.55 (Pro-2), 57.76 (Pro-6), 64.09 (Pro-5), 65.51 (CH of fc), 67.01 (CH of fc), 68.16 (d, $^1J_{PC}$ = 62 Hz, C^{ipso}-P of fc), 68.28 (CH of fc), 68.36 (CH of fc), 72.72 (d, $^3J_{PC}$ = 6 Hz, CH of fc), 74.21 (d, $^3J_{PC}$ = 3 Hz, CH of fc), 74.26 (d, $^2J_{PC}$ = 11 Hz, CH of fc), 79.58 (d, $^2J_{PC}$ = 22 Hz, CH of fc), 101.71 (d, $^4J_{PC}$ = 1 Hz, C^{ipso}-N of fc), 128.17 (d, J_{PC} = 12 Hz, CH of PPh_2), 128.69 (d, J_{PC} = 11 Hz, CH of PPh_2), 130.79 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 131.30 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 130.86 (d, $^1J_{PC}$ = 54 Hz, C^{ipso} of PPh_2), 131.57 (d, J_{PC} = 10 Hz, CH of PPh_2), 132.42 (d, $^1J_{PC}$ = 57 Hz, C^{ipso} of PPh_2), 134.49 (d, J_{PC} = 11 Hz, CH of PPh_2), 196.08 (d, $^3J_{PC}$ = 4 Hz, carbene). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz): δ 18.8 (s). IR (Nujol) ν_{max}/cm^{-1}: 3072 w, 3049 w, 1497 s (carbene), 1436 s, 1325 w, 1269 m, 1168 m, 1098 m, 1067 w, 1032 m, 999 w, 933 w, 825 m, 746 s, 694 s, 629 m, 529 m, 508 s, 481 s, 440 m. MS ESI+: m/z 583 ([M − HCl − Cl]$^+$), 619 ([M − Cl]$^+$). MS ESI−: m/z 691 ([M + Cl]$^-$). Anal. Calcd for $C_{28}H_{27}Cl_2FeN_2PPd$ (655.6): C, 51.29%; H, 4.15%; N, 4.27%. Found: C, 51.27%; H, 4.00%; N, 4.12%.

Analytical data for (S,S_p)-7. $[\alpha]^{20}_{589}$ = +277 (c = 0.38, CH_2Cl_2). ^{1}H NMR (CD_2Cl_2, 600 MHz): δ 0.27 (qd, J_{HH} = 11.1 Hz, 8.3 Hz, 1 H, Pro), 1.52 (dtdd, J_{HH} = 13.2 Hz, 8.4 Hz, 3.5 Hz, 1.4 Hz, 1 H, Pro), 1.72 (m, 1 H, Pro), 1.82 (dddt, J_{HH} = 12.9 Hz, 10.9 Hz, 10.0 Hz, 7.7 Hz, 1 H, Pro), 3.29 (dt, J_{HH} = 11.6 Hz, 8.3 Hz, 1 H, Pro), 3.48 (t, J_{HH} = 10.4 Hz, 1 H, Pro), 3.62 (ddd, J_{HH} = 11.6 Hz, 10.1 Hz, 3.4 Hz, 1 H, Pro), 3.76 (td, J_{HH} = 10.5 Hz, 1.4 Hz, 1 H, Pro), 4.13 (qd, J_{HH} = 10.4 Hz, 5.7 Hz, 1 H, Pro), 4.39 (td, J = 2.6 Hz, 1.4 Hz, 1 H, CH of fc), 4.43 (td, J = 2.6 Hz, 1.4 Hz, 1 H, CH of fc), 4.67 (m, 2 H, CH of fc), 4.71 (td, J = 2.6 Hz, 1.4 Hz, 1 H, CH of fc), 4.79 (m, 1 H, CH of fc), 5.44 (dt, J = 2.8 Hz, 1.7 Hz, 1 H, CH of fc), 5.98 (ddtd, $^3J_{PH}$ = 4.0 Hz, J_{HH} = 2.7 Hz, 1.3 Hz, 0.5 Hz, 1 H, CH of fc), 7.36−7.40 (m, 2 H, PPh_2), 7.43−7.49 (m, 4 H, PPh_2), 7.67−7.76 (m, 4 H, PPh_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 151 MHz): δ 25.84 (Pro), 30.44 (Pro), 46.27 (Pro), 58.47 (Pro), 64.86 (Pro), 65.19 (d, $^1J_{PC}$ = 62 Hz, C^{ipso}-P of fc), 65.30 (CH of fc), 67.03 (CH of fc), 67.06 (CH of fc), 73.35 (d, $^3J_{PC}$ = 6 Hz, CH of fc), 74.30 (d, $^2J_{PC}$ = 12 Hz, CH of fc), 74.44 (d, $^3J_{PC}$ = 3 Hz, CH of fc), 79.84 (d, $^2J_{PC}$ = 23 Hz, CH of fc), 102.55 (d, $^4J_{PC}$ = 1 Hz, C^{ipso}-N of fc), 128.15 (d, J_{PC} = 12 Hz, CH of PPh_2), 129.30 (d, J_{PC} = 10 Hz, CH of PPh_2), 130.99 (d, $^4J_{PC}$ = 4 Hz, CH^{para} of PPh_2), 131.15 (d, $^1J_{PC}$ = 54 Hz, C^{ipso} of PPh_2), 131.34 (d, $^4J_{PC}$ = 3 Hz, CH^{para} of PPh_2), 131.99 (d, J_{PC} = 9 Hz, CH of PPh_2), 132.77 (d, $^1J_{PC}$ = 55 Hz, C^{ipso} of PPh_2), 134.53 (d, J_{PC} = 11 Hz, CH of PPh_2), 190.88 (carbene). ^{31}P{^{1}H} NMR (CD_2Cl_2, 162 MHz): δ 16.3 (s). IR (Nujol) ν_{max}/cm^1 3068 w, 3042 w, 1495 s (carbene), 1437 s, 1307 w, 1265 m, 1168 m, 1097 m, 1067 w, 1031 m, 999 w, 937 w, 888 w, 824 m, 746 s, 695 s, 628 s, 540 w, 529 m, 508 s, 481 s, 442 m. MS ESI+: m/z 583 ([M − HCl − Cl]$^+$). Anal. Calcd for $C_{28}H_{27}Cl_2FeN_2PPd$ (655.6): C, 51.29%; H, 4.15%; N, 4.27%. Found: C, 51.46%; H, 4.26%; N, 4.08%.

Catalytic Borylation of Aryl Bromides. A Schlenk tube was charged successively with aryl bromide (1.0 mmol), bis(pinacolato)-diboron (304 mg, 1.2 mmol), the catalyst (0.01 mmol), base (2.0 mmol), and anhydrous isopropanol (or other solvent during the screening experiments; 4 mL). After degassing for five freeze−pump−thaw cycles, the mixture was transferred into an oil bath kept at 85 °C. After heating for 6 h, the reaction mixture was cooled to room temperature and diluted with ethyl acetate (5 mL) and water (10 mL). The organic layer was separated and the aqueous residue extracted with ethyl acetate (3× 5 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated. In the screening experiments, anisole (108 mg, 1.0 mmol) was added as an internal standard, and the mixture was analyzed by NMR spectroscopy. During the preparative experiments, the filtered reaction mixture was evaporated, and the crude product was purified by column chromatography over silica gel using hexane−ethyl acetate mixtures as the eluent (30:1 to 3:1 depending on the compound).

X-ray Crystallography. Full-set diffraction data were collected with a Bruker D8 VENTURE Kappa diffractometer equipped with a Duo PHOTON100 detector, a IμS microfocus sealed tube source, and a Cryostream cooler at 150 K using Mo Kα radiation. The structures were solved by direct methods (SHEXLT-2014[38]) and refined by least-squares against F^2 with SHELXL-2014 or SHELXL-2017.[39] All non-hydrogen atoms were refined with anisotropic displacement parameters. The NH hydrogens were located on difference electron density maps and refined as riding atoms with U_{iso}(H) set to 1.2U_{eq}(N). Hydrogens residing on the carbon atoms (CH_n) were included in their theoretical positions and refined similarly. Particular details on structure refinement are as follows. Compound **2a** crystallizes as a chloroform solvate and with two structurally independent complex molecules (space group $P\bar{1}$). Two of the solvent molecules in the asymmetric unit were refined, but the remaining ones, disordered within large structural voids (approximately 12% of the unit cell volume), could not be adequately modeled and, hence, were removed from the refinement by PLATON SQUEEZE.[40] One of the solvating methanol molecules in the structure of **4a**·2MeOH and the solvent molecules in the structures of **5b**·CH_2Cl_2 and **6b**·1/2CH_2Cl_2 were similarly treated.

Selected crystallographic data and structure refinement parameters are outlined in the Supporting Information (Table S1). PLATON[41] was used to create all structural diagrams and to perform geometric calculations. The numerical values are rounded to one decimal place of their estimated standard deviations (ESDs). Parameters pertaining to atoms in constrained positions are presented without ESDs.

DFT Calculations. Theoretical calculations were performed using the Gaussian 09 program package.[42] The reported energies correspond to Gibbs free energies obtained from full geometry optimizations (starting from atomic coordinates determined by X-ray diffraction analysis where possible) using meta-GGA (TPSS)[43] and hybrid (B3LYP,[44,45] PBE0[46]) density functionals in conjunction with the Stuttgart effective core potential[47] used for the transition metals (Fe, Pd) and with the def2-TZVP[48] basis set used for the remaining elements (C, H, N, P, Cl) with added Grimme's D3 dispersion correction.[49] The solvent effects (dichloromethane) were approximated using the polarized continuum model (PCM).[50] Topological analysis of the electron density according to the atoms in molecules (AIM) method[51] and orbital composition analysis were performed using the Multiwfn software package (version 3.6).[52] Molecular orbitals were visualized using the Avogadro program.[53]

■ ASSOCIATED CONTENT

Supporting Information

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Organometallics XXXX, XXX, XXX−XXX

Further experimental details, characterization data for the coupling products **9**, additional structural diagrams, summary of the crystallographic data and structure refinement parameters, as well as copies of the NMR spectra (PDF)

Cartesian coordinates of the DFT optimized structures (XYZ)

Accession Codes

CCDC 1922546−1922553 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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