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# Imidazole Phosphines: Synthesis, Reaction Chemistry, and Their Use in Suzuki *C,C* Cross-Coupling Reactions

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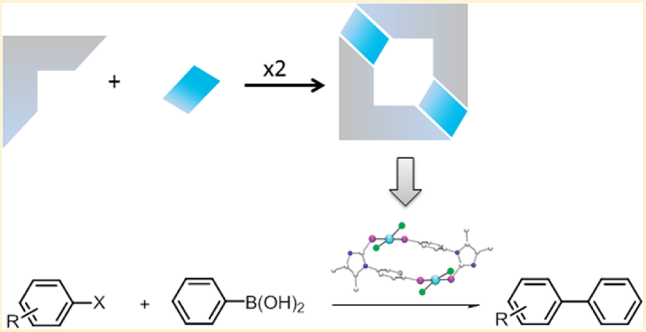
Supporting Information

**ABSTRACT:** A straightforward consecutive synthesis methodology for the preparation of phosphino imidazoles 1-(4-$PR_2$-$C_6H_4$)-4,5-$Me_2$-1*H*-$C_3HN_2$ (**4a**, R = $C_6H_5$; **4b**, R = $^cC_6H_{11}$) and 1-(4-$PR_2$-$C_6H_4$)-2-$PR'_2$-4,5-$Me_2$-1*H*-$C_3N_2$ (R = $C_6H_5$: **6a**, R′ = $C_6H_5$; **6b**, R′ = $^cC_6H_{11}$; **6c**, R′ = $^cC_4H_3O$; R = $^cC_6H_{11}$: **6d**, R′ = $C_6H_5$; **6e**, R′ = $^cC_6H_{11}$; **6f**, R′ = $^cC_4H_3O$) is presented. Phosphino imidazoles **6a−f** were reacted with $[PdCl_2(SEt_2)_2]$ (**7**), giving $[Pd(1\text{-}(4\text{-}PR_2\text{-}C_6H_4)\text{-}2\text{-}PR'_2\text{-}4,5\text{-}Me_2\text{-}1H\text{-}C_3N_2)\text{-}Cl_2]_2$. Single crystals of $[Pd(1\text{-}(4\text{-}P(C_6H_5)_2\text{-}C_6H_4)\text{-}2\text{-}P(^cC_4H_3O)_2\text{-}4,5\text{-}Me_2\text{-}1H\text{-}C_3N_2)Cl_2]_2$ (**8**) suitable for single-crystal X-ray structure analysis could be obtained by using the synthesis-*cum*-diffusion strategy, confirming the formation of a neutral 18-membered $Pd_2P_4$ cycle with two *trans*-configurated palladium centers. A $Pt_4P_4$ cyclic compound, accessible by molecular recognition, was obtained via treatment of $[Pt(dppf)(C{\equiv}C\text{-}C_6H_4\text{-}4\text{-}P(C_6H_5)_2)_2]$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) (**11**) with $[PtCl_2(SEt_2)_2]$ (**12**). The structure of **13** in the solid state was confirmed by crystal structure determination, proving the formation of a neutral molecular square composed of Pt(dppf) and $PtCl_2$ corner units and 4-$(C_6H_5)_2$P-$C_6H_4$-C≡C linkers. In addition, compounds **6a−f** were applied in the palladium-promoted Suzuki cross-coupling of 2-bromotoluene with phenylboronic acid using potassium carbonate as base. All *in situ* generated phosphino imidazole palladium species showed high catalytic activity at which the diphosphino systems featuring phenyl and cyclohexyl groups achieved the best results. Additionally, phosphine **6d** was applied in the coupling of 4-chlorotoluene with phenylboronic acid and in the synthesis of sterically hindered biaryls under mild reaction conditions, showing an excellent performance. In comparison with other catalytically active species, equal or higher productivities were obtained using lower catalyst loadings and lower temperatures.




## INTRODUCTION

Phosphino imidazoles represent an interesting family of molecules due to their ambivalent donor character (*P,N*), allowing their coordination to hard or soft transition metal fragments.[1] They can be used, for example, as easily tunable ligands with good performance in palladium-catalyzed *C,C* couplings,[1a,d,2] as structural elements of ionic liquids in two-phase catalytic reactions, allowing facile recycling,[1b,d,e,2a,c,3] or as model system for mimicking the catalytically active site in bioinorganics.[1c,4] In contrast to monophosphino imidazoles, diphosphino imidazoles were investigated in combination with chirality.[2d,5]

Discrete molecular architectures can be designed and synthesized by molecular recognition using, for example, organic and metal−organic or organometallic compounds as building blocks containing the structural information to construct the appropriate self-assembled 2D or 3D architectures.[6] Such structures include for instance molecular rods, squares, hexagons, and boxes of which the appropriate squares featuring transition metal groups were among the first successfully synthesized examples.[6f,g] *Exo*-bidentate metal−organic units including nitrogen donors and mainly palladium and platinum metals have been employed as edges, while as linking components generally organic units are applied.[6] Examples of metallo-supramolecular squares are $[\{Pt(\mu\text{-}4,4'\text{-}bpy)(dppp)\}_4]^{8+}$ [6f] or $[\{Pt\text{-}\mu\text{-}C{\equiv}C\text{-}C{\equiv}C)(dcpe)\}_4]^{4+}$[7] (dppp = bis(diphenylphosphino)propane, dcpe = bis(dicyclohexylphoshino)ethane). Applications of such metallamacrocycles include homogeneous catalysis[8] and host−guest chemistry.[6i]

This prompted us to combine the two topics phosphino imidazoles and metallamacrocycles. In addition, the use of the appropriate phosphines in Suzuki *C,C* cross-coupling reactions is reported.

## RESULTS AND DISCUSSION

**Synthesis and Characterization of Phosphino Imidazoles and Metallamacrocycles.** Diphosphino imidazoles 1-

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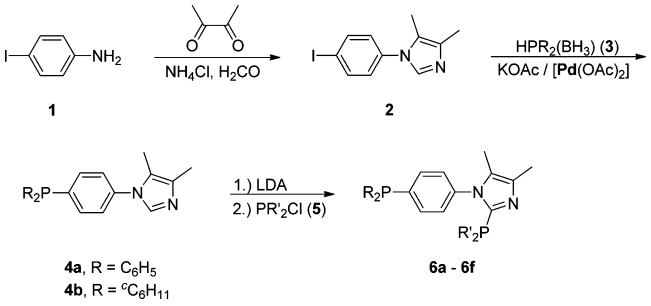
(4-$PR_2$-$C_6H_4$)-2-$PR'_2$-4,5-$Me_2$-1*H*-$C_3N_2$ (R = $C_6H_5$: **6a**, R′ = $C_6H_5$; **6b**, R′ = $^cC_6H_{11}$; **6c**, R′ = $^cC_4H_3O$; R = $^cC_6H_{11}$; **6d**, R′ = $C_6H_5$; **6e**, R′ = $^cC_6H_{11}$; **6f**, R′ = $^cC_4H_3O$) were accessible in a consecutive reaction sequence as shown in Scheme 1. Molecule **2** is remarkably sensitivity toward light, and hence rapid workup is highly recommended.

**Scheme 1. Synthesis of Diphosphino Imidazoles 6a−f**[a]



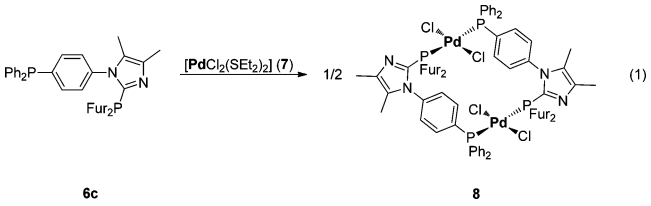

[a]LDA = $LiN(^iC_3H_7)_2$.

Palladium-promoted Stelzer coupling[9] of 1-(4-I-$C_6H_4$)-4,5-$Me_2$-1*H*-$^cC_3HN_2$ (**2**) with $PR_2H(BH_3)$ (**3a**, R = $C_6H_5$; **3b**, R = $^cC_6H_{11}$) gave 1-(4-$PR_2$-$C_6H_4$)-4,5-$Me_2$-1*H*-$^cC_3HN_2$ (**4a**, R = $C_6H_5$; **4b**, R = $^cC_6H_{11}$), which on deprotonation with $LiN(^iC_3H_7)_2$ followed by subsequent treatment with $PR'_2Cl$ (**5a**, R = $C_6H_5$; **5b**, R = $^cC_6H_{11}$; **5c**, R = $^cC_4H_3O$) produced colorless diphosphines **6a−f** (Table 1, Experimental Section). Noteworthy is the high reactivity of phosphines **4** and **6** toward oxygen. They are rapidly oxidized to the respective phosphine oxides when exposed to air, solutions more quickly than solid materials. This also is reflected by the somewhat low yields characteristic for **4** and **6** (Table 1, Experimental Section).

Phosphines **4** and **6** were characterized by elemental analysis, IR, and NMR ($^1$H, $^{13}$C{$^1$H}, $^{31}$P{$^1$H}) spectroscopy and high-resolution ESI TOF mass spectrometry.

The IR spectra of the mono- and diphosphino imidazoles are less expressive, while NMR spectroscopy is more meaningful. Very characteristic is the sp$^2$-hybridized CH imidazole proton signal at ca. 7.5 ppm for **4a** and **4b**, which upon substitution by the $PR'_2$ group (**6a−f**) disappears, allowing the monitoring of the reaction progress. This also is possible using $^{13}$C{$^1$H} NMR spectroscopy because a shift of the imidazole carbon atom in position 2 from 137 ppm in **4** (C−H) to 140−145 ppm in **6** (C−$PR'_2$; $^1J_{CP}$ = 2−15 Hz) occurs (Experimental Section). A further feature of **6a−f**, as compared to **4**, is the appearance of a doublet of doublets (i.e., **6a**: $^3J_{CP}$ = 3.1 Hz, $^4J_{PC}$ = 2.8 Hz) for the *meta*-positioned phenylene C−H unit, due to its coupling with both the $PR_2$ and the $PR'_2$ building blocks. In addition, $^{31}$P{$^1$H} NMR spectroscopy is an efficient tool to describe the introduction of a second phosphino moiety. While for **4** only one resonance signal is observed at 2.7 (**4a**) and −5.9 (**4b**) ppm, respectively, for **6a−f** two resonances between −71.7 and 2.6 ppm are characteristic, whereas the signal of the $PR'_2$ unit always appears at higher field. Nevertheless, the phosphino groups do not show phosphorus−phosphorus couplings.

Phosphino imidazoles **6a−f** can be applied in the Suzuki *C,C* cross-coupling of 2-bromotoluene with phenylboronic acid (*vide infra*) as well as in the synthesis of palladamacrocycles (reaction 1). Molecules **6a−f** react quantitatively and rapidly




with $[PdCl_2(SEt_2)_2]$ (**7**) at ambient temperature to give air- and moisture-stable yellow complexes of type [Pd(1-(4-$PR_2$-$C_6H_4$)-2-$PR'_2$-4,5-$Me_2$-1*H*-$C_3N_2$)$Cl_2$]$_2$. Within this reaction, even using different reaction conditions, always nonsoluble materials were obtained and hence characterization is limited. However, with **6c** as phosphino source single crystals of **8** suitable for single X-ray structure studies could be obtained, which allowed determining the structure of this complex in the solid state (Figure 1).

The very poor solubility of **8** even in common polar organic solvents precluded any reasonable NMR data. However, suitable crystals for single X-ray structure analysis were obtained by the one-step synthesis-*cum*-diffusion strategy at ambient temperature so that crystals could be formed in a slow reaction (*vide supra*). These crystals were subjected to single-crystal X-ray structure analysis. The molecular structure of **8** is shown in Figure 1. Important bond lengths, bond angles, and torsion angles are summarized in the caption of Figure 1. For crystal and structure refinement data see the Experimental Section.

Cyclic **8** crystallizes in the monoclinic space group $P2_1/c$. In its solid state it forms a dimeric *trans*-palladium complex with two bidentate imidazole ligands bridging two $PdCl_2$ units, forming an 18-membered metallacycle. Compound **8** possesses a crystallographically imposed inversion symmetry with the inversion center in the middle of Pd1 and Pd1A (Figure 1). The coordination at Pd is distorted square-planar. The phenylene groups are oriented parallel to each other with an interplanar distance of ca. 6.2 Å. As expected, the imidazole unit shows planarity (rms deviation 0.0094 Å), and the phenylene moiety is rotated by 70.3(5)° out of the plane of the imidazole entity. Therefore, the molecule is not planar but exhibits a structure similar to cyclophanes.[10a] The Pd···Pd distance is 6.519 Å, alluding that no direct Pd−Pd contact exists. Similar distances have been observed for [Pd(2,5-($PC_6H_5$)$_2$)$_2$-$C_4H_2S$)$Cl_2$]$_2$.[10b] All other bond lengths and angles correspond to related molecules, i.e., [Pd(1,3-*i*-$Pr_2$-2-$PPh_2$-4,5-$Me_2$-$C_3N_2$)-$Cl_3$][11] and [Pd(2,5-($PPh_2$)$_2$-$C_4H_2S$)$Cl_2$]$_2$.[10b]

**Table 1. Synthesis of Diphosphino Imidazoles 6a−f**

| compd | R | R′ | yield/%[a] | compd | R | R′ | yield/%[a] |
|---|---|---|---|---|---|---|---|
| **6a** | $C_6H_5$ | $C_6H_5$ | 57 | **6d** | $^cC_6H_{11}$ | $C_6H_5$ | 60 |
| **6b** | $C_6H_5$ | $^cC_6H_{11}$ | 50 | **6e** | $^cC_6H_{11}$ | $^cC_6H_{11}$ | 46 |
| **6c** | $C_6H_5$ | $^cC_4H_3O$ | 64 | **6f** | $^cC_6H_{11}$ | $^cC_4H_3O$ | 65 |

[a]Based on **4a** or **4b**.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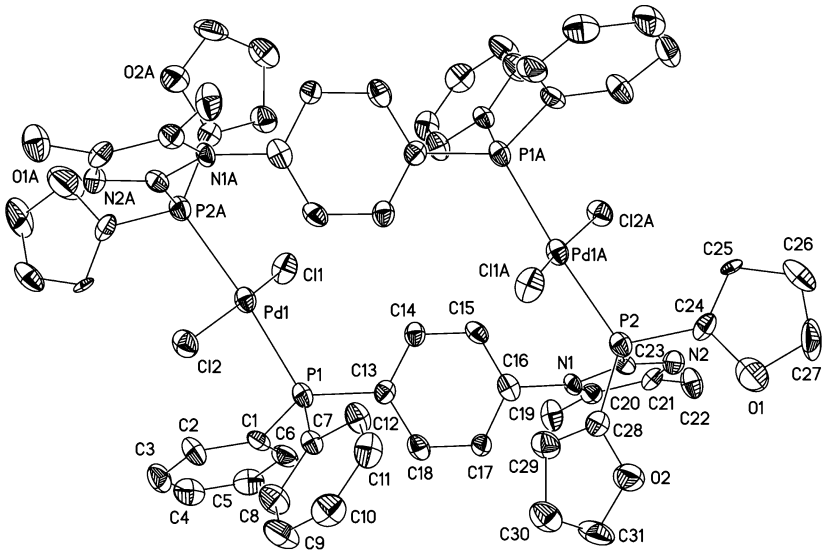
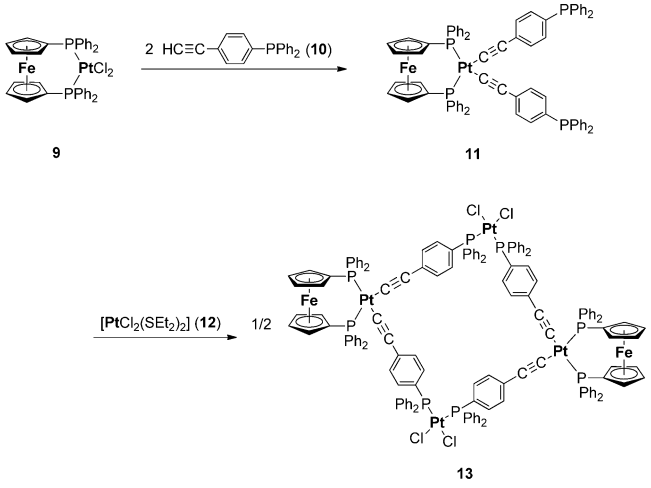



**Figure 1.** ORTEP diagram (50% probability level) of the molecular structure of **8** crystallized from dichloromethane, with the atom-numbering scheme. All hydrogen atoms have been omitted for clarity. Selected bond lengths (Å), angles (deg), and torsion angles (deg): Pd1−P1 = 2.3127(12), Pd1A−P2 = 2.3171(12), Pd1−Cl1 = 2.3008(11), Pd1−Cl2 = 2.3055(10), Pd1−P2A = 2.3171(12), C1−P1 = 1.805(4), C7−P1 = 1.814(4), C13−P1 = 1.823(4), C23−P2 = 1.796(4), C24−P2 = 1.780(5), C28−P2 = 1.799(4); Cl1−Pd1−Cl2 = 168.69(4), Cl1−Pd1−P1 = 90.80(4), Cl2−Pd1−P1 = 89.14(4), Cl1−Pd1−Cl2A = 93.61(4), Cl2, Pd1−P2A = 85.99(4), P1−Pd1−P2A = 174.79(4); C15−C16−N1−C23 = 70.3(5), C13−P1−Pd1−Cl1 = 45.28(16). (Symmetry generated atoms are indicated by the suffix A; symmetry code: $-x+2$, $-y$, $-z+1$.)

Supramolecular chemistry also allows the synthesis of a platinum-molecular square, as given in the preparation of **13** (Scheme 2). Treatment of [Pt(dppf)$Cl_2$] (dppf = 1,1′-bis(diphenylphosphino)ferrocene) (**9**) and P($C_6H_5$)$_2$($C_6H_4$-4-C≡CH) (**10**) produced the bis(alkynyl)platinum complex [Pt(dppf)(C≡C-$C_6H_4$-4-P$Ph_2$)$_2$] (**11**) (Scheme 1). The chelating ferrocenyl phosphine was used to enforce the required *cis*-geometry at the platinum atom. Heterobimetallic **11** produced upon reaction with [Pt($SEt_2$)$_2$$Cl_2$] (**12**) via self-assembly the neutral tetranuclear molecular square **13**. Appropriate workup gave **13** in an overall yield of 36% (Experimental Section). Yellow **13** is poorly soluble in polar and nonpolar solvents, and it is stable toward air and moisture. The neutral tetraplatinum square **13** possesses alternating edges composed of Pt(dppf) and $PtCl_2$ moieties, which are connected by linear alkynyl phosphine units 4-($C_6H_5$)$_2$P-$C_6H_4$-C≡C.

**Scheme 2. Synthesis of the Platinum-Molecular Square 13 from 9**




The organometallic bis(alkynyl) platinum complex **11** and square **13** were characterized by elemental analysis, spectroscopy (IR; $^1$H, $^{13}$C{$^1$H}, $^{31}$P{$^1$H} NMR), and single-crystal X-ray structure analysis (Figure 2 (**11**), Figure 3 (**13**)).

Heterobimetallic **11** shows from the spectroscopic point of view no peculiarities (Experimental Section). Nevertheless, the 4-($C_6H_5$)$_2$P-$C_6H_4$-C≡C groups are best suited to monitor the progress of the reaction of **11** with **12** to form **13** since a shift of the phosphorus signal from −6.6 ppm in **11** to 14.7 ppm in **13** ($PtCl_2$ edge fragment) occurs in the $^{31}$P{$^1$H} NMR spectrum. Compounds **11** and **13** show a second phosphorus signal at 13.6 ppm, which can be assigned to the Pt(dppf) building block with a characteristic $^1J_{^{195}Pt-^{31}P}$ coupling constant of 2380 Hz. The phosphorus−platinum coupling constant $^1J_{^{195}Pt-^{31}P}$ = 3673 Hz ($PtCl_2$) confirms the expected *cis*-arrangement at the platinum(II) center. The $^1$H NMR spectra of **11** and **13** are easier to interpret due to their symmetrical structure (Figures 2 and 3) exhibiting the expected signals of the organic groups with remarkable AA′XX′ patterns for the phenylene and the cyclopentadienyl groups. However, $^{13}$C{$^1$H} NMR spectroscopy delivered no usable information due to the poor solubility of **13**. The successful formation of **11** can be IR spectroscopically controlled by the disappearance of the alkynyl C−H stretching frequency through the course of the reaction of **9** with **10** (Experimental Section). The alkynyl units in **11** and **13** are characterized by strong C≡C vibrations at 2112 (**10**) and 2114 cm$^{-1}$ (**11**, **13**), respectively.

Single crystals of **11** and **13** could be grown by slow diffusion of *n*-hexane into a dichloromethane solution containing **11** at ambient temperature or slowly cooling a saturated dichloromethane−**13** solution from 50 °C to ambient temperature. The molecular structure of **11** in the solid state is shown in Figure 2, while that of **13** is depicted in Figure 3. Important bond lengths (Å) and bond angles (deg) are summarized in the captions of Figures 2 and 3, respectively. For crystal and structure refinement data see the Experimental Section.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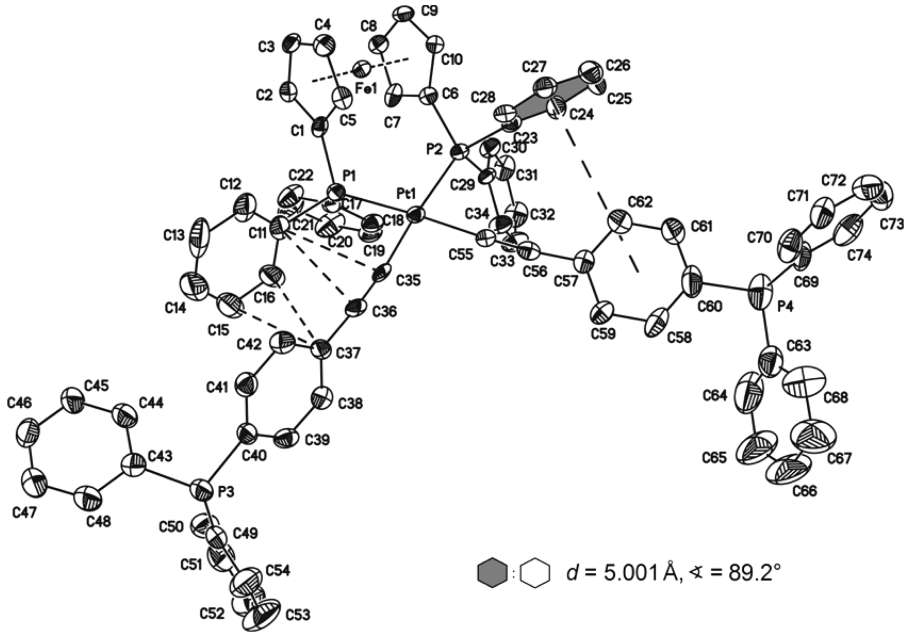
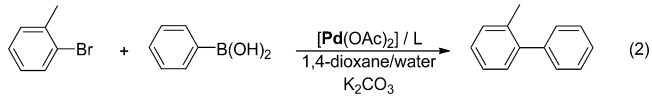



**Figure 2.** ORTEP diagram (50% probability level) of the molecular structure of **11** with the atom-numbering scheme. All hydrogen atoms and one molecule of chloroform have been omitted for clarity. The T-shaped $\pi,\pi$ interactions between the aromatic $C_6$ rings C23−C28 and C57−C62 are indicated with a dashed line, whereby *d* refers to the geometrical centroid to geometrical centroid distance and ∠ to the interplanar angle. Further $\pi$ interactions are indicated by dashed lines; carbon−carbon distances are in the range 3.109 (C11−C35) to 3.495 Å (C16−C37). Selected bond lengths (Å) and angles (deg): C35−C36 = 1.219(9), C55−C56 = 1.186(9), C35−Pt1 = 1.985(7), C55−Pt1 = 2.013(7), P1−Pt1 = 2.3010(18), P2−Pt1 = 2.3287(17), D1−Fe1 = 1.643, D2−Fe1 = 1.642; C36−C35−Pt1 = 174.1(6), C56−C55−Pt1 = 177.5(6), C35−Pt1−C55 = 90.4(3), C35−Pt1−P1 = 86.92(18), C55−Pt1−P1 = 177.06(19), C35−Pt1−P2 = 175.86(19), C55−Pt1−P2 = 85.60(19), P1−Pt1−P2 = 97.11(6), D1−Fe1−D2 = 177.5 (D1, D2 = denote the centroids of $C_5H_4$ at Fe1).

Complex **11** crystallizes in the monoclinic space group $C_2/c$ and exhibits a square-planar geometry around Pt1 (rms deviation 0.0062 Å, highest deviation from planarity observed for Pt1 with −0.0156 Å) with a P1−Pt1−P2 bite angle of 97.11(6)° and a C35−Pt1−C55 angle of 90.4(3)°. The ferrocene moiety exhibits a staggered conformation (−35.2°), and the D1−Fe1 and D2−Fe1 separations at 1.642(3) and 1.640(3) Å (D1, D2 = centroids of $C_5H_4$) are similar to those of related compounds.[12a] The cyclopentadienyl rings are 5.7(5)° deviated from parallelism. The Pt−C≡C−$C_{Ph}$ units are almost linear, with Pt1−C35−C36, C35−C36−C37, Pt1−C55−C56, and C55−C56−C57 angles of 174.1(6)°, 173.8(7)°, 177.5(6)°, and 172.0(8)° (Figure 2). The Pt−$C_{C\equiv C}$ distances of 1.985(7) and 2.013(7) Å and the C≡C bond lengths of 1.219(9) and 1.186(9) Å reflect the formal bond order of these units.[6b,12a] Furthermore, complex **11** exhibits intramolecular T-shaped and sandwich $\pi,\pi$ interactions (Figure 2).[12b] The C35−Pt1−C55 angle (see above) provides the best precondition for the formation of molecular squares.

Complex **13** crystallizes in the monoclinic space group $P_2/n$ and possesses a crystallographically imposed inversion symmetry with the inversion center in the middle between the platinum atoms Pt1 and Pt1A as well as Pt2 and Pt2A, respectively (Figure 3). The 32-membered metallamacrocycle consists of four platinum atoms at the corners, of which two are coordinated by a chelating dppf and two monodentate $PPh_2$ moieties. The geometry around Pt1 and Pt2 is distorted square planar with C35−Pt1−C74, P1−Pt1−P2, P4−Pt2−P3, and Cl1−Pt2−Cl2 angles of 85.7(7)°, 98.24(17)°, 96.44(18)°, and 86.20(18)° (Pt1: rms deviation 0.0250 Å, highest deviation from planarity observed for Pt1 of 0.0484 Å; Pt2: rms deviation 0.1528 Å, highest deviation from planarity observed for P3 of 0.1890 Å). The Pt-C≡C−$C_{Ph}$ units are essentially linear, with Pt1−C35−C36, C35−C36−C37, Pt1−C74−C73, and C74−C73−C70 angles of 177.4(17)°, 169(2)°, 173(2)°, and 174.1(18)° and C≡C distances of 1.23(2) and 1.14(2) Å, respectively. The ferrocenyl moieties exhibit a staggered conformation (−35.8°) with the cyclopentadienyl rings oriented virtually parallel to each other (4.6°). In addition, complex **13** exhibits intramolecular T-shaped, parallel-displaced, and sandwich $\pi,\pi$ interactions (Figure 3).[12b] The Pt1···Pt1A and Pt2···Pt2A distances are 11.9350(4) and 16.2205(4) Å, respectively, allowing, for example, the placement of small molecules or group 11 cations as already described for $[\{Pt\text{-}\mu\text{-}C\equiv C\text{-}C\equiv C)(dppe)\}_4]$ (dppe = bis(diphenylphosphine)ethane).[6b] Complex **13** crystallizes with 11 molecules of chloroform as packing solvent, of which four are located in the cavity. However, the molecule is not planar due to the geometry of the phosphorus atoms P3 and P4. All other structural parameters are similar to those of related molecules, e.g., $[Pt(dppf)(C\equiv CPh)_2]$[12a] and $[\{Pt\text{-}\mu\text{-}C\equiv C\text{-}C\equiv C)\text{-}(dcpe)\}_4]^{4+}$[7] (dcpe = bis(dicyclohexylphoshino)ethane).

**Suzuki *C,C* Cross-Coupling Reactions.** Initially, mono- (**4a**, **4b**) and diphosphino imidazoles (**6a**−**f**) were applied in the palladium-mediated Suzuki−Miyaura coupling of 2-bromotoluene with phenylboronic acid, *in situ* generating the catalytically active species by applying mixtures of $[Pd(OAc)_2]$ and **4a** or **4b** (ratio 1:2) or **6a**−**f** (ratio 1:1) (reaction 2) to test



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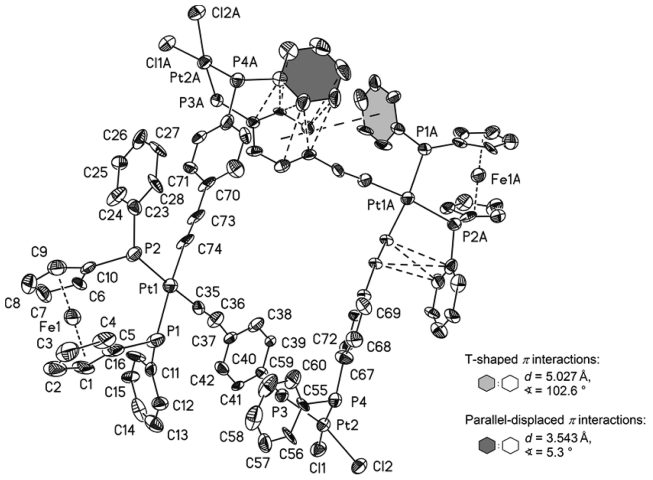


**Figure 3.** ORTEP diagram (50% probability level) of the molecular structure of **13** with the atom-numbering scheme. All hydrogen atoms, the packing solvent chloroform, and the phosphorus-bonded phenyl groups, which are not involved in $\pi,\pi$ interactions, have been omitted for clarity. The T-shaped $\pi,\pi$ interactions between the aromatic $C_6$ rings C11−C16 and C37−C42 are indicated with a dashed line, at which $d$ refers to the geometrical centroid to geometrical centroid distance and $\angle$ to the interplanar angle. Further parallel-displaced and sandwich $\pi,\pi$ interactions are indicated by dashed lines. Carbon−carbon distances are in the range 3.024 (C23−C74) to 3.502 Å (C42−C58). Selected bond lengths (Å) and angles (deg): C35−C36 = 1.23(2), C73−C74 = 1.14(2), C35−Pt1 = 1.996(17), C74−Pt1 = 2.030(18), P1−Pt1 = 2.290(5), P2−Pt1 = 2.311(4), P3−Pt2 = 2.264(5), P4−Pt2 = 2.239(6), Cl1−Pt2 = 2.352(5), Cl2−Pt2 = 2.361(5), D1−-Fe1 = 1.646, D2−Fe1 = 1.641; C36−C35−Pt1 = 177.4(17), C73−C74−Pt1 = 173(2), C35−Pt1−C74 = 85.7(7), C35−Pt1−P1 = 87.0(5), C74−Pt1−P1 = 172.4(5), C35−Pt1−P2 = 173.2(6), C74−Pt1−P2 = 88.9(5), P1−Pt1−P2 = 98.24(17), P4−Pt2−P3 = 96.44(18), P4−Pt2−Cl1 = 173.00(17), P3−Pt2−Cl1 = 88.51(19), P4−Pt2−Cl2 = 90.01(18), P3−Pt2−Cl2 = 166.45(18), Cl1−Pt2−Cl2 = 86.20(18), D1−Fe1−D2 = 178.9. (D1, D2 = denote the centroids of $C_5H_4$ at Fe1; symmetry -generated atoms are indicated by the suffix A; symmetry codes: $-x+1/2, y, -z+3/2$; $-x+3/2, y, -z+3/2$.)

the new phosphino imidazoles. The catalytic reactions were carried out in 1,4-dioxane−water mixtures of ratio 2:1 in the presence of potassium carbonate as base at 100 °C using 0.5 mol % of the monophosphine and 0.25 mol % of the appropriate diphosphine, respectively, and 0.25 mol % of the palladium source. Acetylferrocene as standard was added to the appropriate reaction solution to determine the rate of conversion by $^1$H NMR spectroscopy. The obtained conversions equal $^1$H NMR spectroscopic yields and are based on the respective aryl halides.

As it can be seen from Figure 4, all compounds are catalytically active, whereas phosphines **6a−f** are more productive and active than **4a** and **4b**. Due to the more electron-rich and bulky cyclohexyl groups, monophosphine **4b** is more active then **4a**, featuring phenyl groups. While **4b** produces 2-methylbiphenyl in a yield of 59%, with **4a** only a conversion of 18% is achieved (Figure 4), which is comparable with the performance of triphenylphosphino ligands in *C,C* couplings.[13]

In general, the phenyl (**6a**,**b**)- and cyclohexyl (**6d**,**e**)-functionalized diphosphino systems show significantly higher activity and productivity than the furyl (**6c**,**f**) derivatives. Furthermore, from Figure 4 it can be seen that the performance of the catalysts **6c** and **6f** with furyl-substituted diphosphines is similar to the catalytic behavior of the complexes carrying monophosphines **4a** and **4b**. This result can be explained by the weak $\sigma$-donating ability of the furyl phosphino group and hence has a smaller influence on the active species. Also, the catalysts based on diphosphines **6a**, **b**, **d**, and **e** show a similar catalytic behavior, reaching 86−100% conversion after 1 h (Figure 4). Apparently, the second phosphino group featuring stronger $\sigma$ donors has a positive effect on the stabilization of the active species visible by the higher activity. However, the difference of the nature of the phosphino group (phenyl vs cyclohexyl) is less decisive. Nevertheless, the catalytic systems featuring phosphines **6d** and **6e** show a somewhat higher activity compared to **6a** and **6b**.

We also investigated the catalytic behavior of our systems (i) in the coupling of nonactivated 4-chlorotoluene with phenylboronic acid using 0.01 mol % $[Pd(OAc)_2]$ and (ii) in the synthesis of sterically hindered biaryls at 50 °C. To achieve comparable results with literature-known systems, we changed to non-aqueous reaction conditions including potassium phosphate as base and toluene as solvent.

From Table 2 it can be seen that the Suzuki coupling of 4-chlorotoluene with phenylboronic acid to give 4-methylbiphenyl using phosphines **4a** and **6b** in combination with $[Pd(OAc)_2]$ gave 64% and 89% conversion, respectively (Table 2, entries 1, 2). Especially diphosphine **6d** (TON: 8900) shows similar results, when compared to the *tert*-butyl-substituted monophosphino benzimidazole (TON: 8600) reported by Beller et al.[2b] and the cyclohexyl phosphino imidazole (TON:

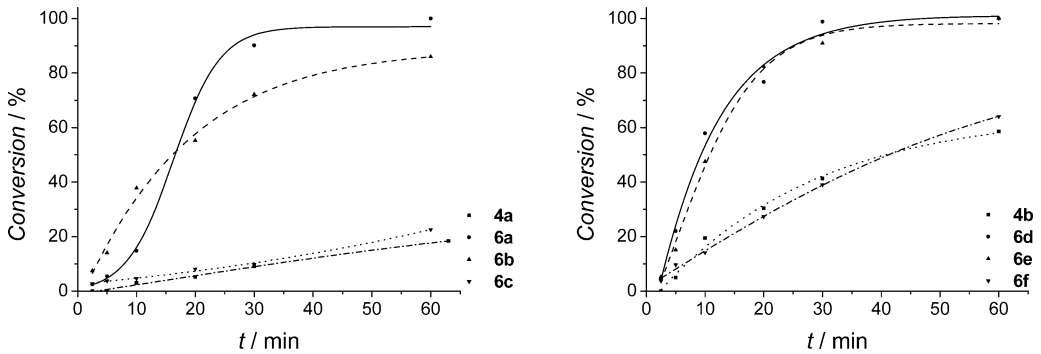


**Figure 4.** Kinetic investigation of **4a** and **6a−c** (left) and **4b** and **6d−f** (right) in the Suzuki−Miyaura *C,C* cross-coupling of 2-bromotoluene with phenylboronic acid to give 2-methylbiphenyl (0.5 mol % mono- or 0.25 mol % diphosphine, 0.25 mol % $[Pd(OAc)_2]$, conversion time 0−60 min); reaction conditions based on ref 14.


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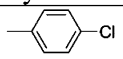
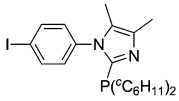
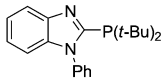
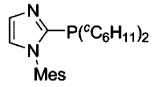
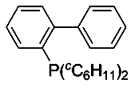
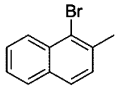
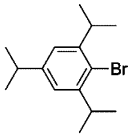
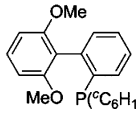
**Table 2. Suzuki Coupling of 4-Chlorotoluene and Sterically Hindered Aryl Bromides**

| Entry | Aryl Halide | Ligand | Catalyst / mol% | Conversion / % | TON |
|---|---|---|---|---|---|
| 1 |  | **4a** | 0.01 | 64 [a)] | 6400 |
| 2 | | **6d** | 0.01 | 89 [a)] | 8900 |
| 3 | |  | 0.01 | 88 [a,b)] | 8800 |
| 4 | |  | 0.01 | 86 [a,c)] | 8600 |
| 5 | |  | 0.01 | 15 – 66 [a,c)] | 1500 – 6600 |
| 6 | |  | 0.05 | 99 [d,e)] | 1860 |
| 7 | | | 0.01 | 47 [d,e)] | 4700 |
| 8 | | $P(t\text{-Bu})_3$ | 0.01 | 92 [d,e)] | 9200 |
| 9 | | $P(n\text{-Bu})Ad_2$ | 0.01 | 94 [d,e)] | 9400 |
| 10 |  | **6d** | 0.05 | 100 [f)] | 2000 |
| 11 |  | **6d** | 0.05 | 100 [f)] | 2000 |
| 12 |  | **6d** | 0.05 | 100 [f)] | 2000 |
| 13 |  | **6d** | 0.05 | 78 [f)] | 1560 |
| 14 | |  | 0.01 | 97 [f,g)] | 9700 |

[a]Reaction conditions:[2b] 4-chlorotoluene (3.0 mmol, 1.0 equiv), phenylboronic acid (4.5 mmol, 1.5 equiv), $K_3PO_4$ (6.0 mmol, 3.0 equiv), toluene (6 mL), $[Pd(OAc)_2]$/phosphine (0.01 mol % [Pd], 0.1 mol % mono- or 0.05 mol % diphosphine), 100 °C, 20 h. [b]Ligand from ref 2f. [c]Ligand from ref 2b. [d]Ligands from ref 15b. [e]Reaction conditions:[15b] 4-chlorotoluene (3.0 mmol, 1.0 equiv), phenylboronic acid (4.5 mmol, 1.5 equiv), $K_3PO_4$ (6.0 mmol, 3.0 equiv), toluene (6 mL), [Pd]:P = 1:2, 100 °C, 20 h. [f]Reaction conditions:[16] aryl halide (1.0 mmol, 1.0 equiv), phenylboronic acid (1.5 mmol, 1.5 equiv), $K_3PO_4$ (3.0 mmol, 3.0 equiv), toluene (2 mL), $[Pd_2(dba)_3]$/phosphine (0.05 mol % [Pd], 0.1 mol % phosphine), 50 °C, 24 h. [g]Ligand from ref 15d, $T$ = 100 °C, 16 h.

8800) reported earlier by our group[2f] (Table 2, entries 3, 4). In summary, excellent results were obtained, when compared to the cyclohexyl-functionalized phosphino imidazole (TON: 1500−6600) by Beller and co-workers[2b] (Table 2, entry 5). Compared to the biphenyl ligand by Buchwald,[15a,d] a significantly higher conversion can be achieved when using 0.01 mol % palladium (Table 2, entry 6).[15b] However, compared to trialkyl phosphino-based catalysts by Fu[15c] and Beller[15b] (Table 2, entries 8, 9), catalyst system **6d**/$[Pd(OAc_2]$ showed under the equivalent reaction conditions a somewhat lower conversion.[15b]

The preparation of sterically hindered biaryls still represents a challenge in organic synthesis, especially under mild reaction conditions. Therefore, we investigated the coupling of *ortho*-substituted aryl bromides with phenylboronic acid in the presence of potassium phosphate as base and $[Pd_2(dba)_3]$ (dba = dibenzylideneacetone) as palladium source at 50 °C. From Table 2 it can be seen that the coupling of aryl bromides with one or two *ortho*-substituents proves successful with a palladium loading of only 0.05 mol % (Table 2, entries 6−9). Even the coupling of the sterically demanding 1,3,5-triisopropyl-2-bromobenzene achieves good results, with a conversion of 78% (Table 2, entry 9). When compared to other catalytic systems suitable for these reactions, e.g., $Fe(\eta^5\text{-}(1\text{-}(4\text{-}t\text{-}Bu\text{-}C_6H_4)\text{-}2\text{-}P(2\text{-}CH_3C_6H_4)_2C_5H_3))(\eta^5\text{-}C_5H_5)$/$[Pd_2(dba)_3]$,[15] only half the amount of palladium is required to achieve quantitative conversion. Compared to the established biphenyl-based catalyst by Buchwald[15d] (Table 2, entry 14),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longer reaction times and higher catalyst loadings are required; however, the catalytic reaction proceeds at considerably lower temperature (50 °C vs 100 °C). Nevertheless, compared to previously reported 1-(4-I-$C_6H_4$)-2-P($^cC_6H_{11}$)$_2$-4,5-$Me_2$-1*H*-$C_3N_2$/[$Pd_2$(dba)$_3$],[2f] no enhanced catalytic activity, based on the second phosphino group, could be observed.

## CONCLUSIONS

It has been shown that mono- and bidentate phosphino imidazoles of type 1-(4-$PR_2$-$C_6H_4$)-4,5-$Me_2$-1*H*-$C_3HN_2$ (R = $C_6H_5$, $^cC_6H_{11}$) and 1-(4-$PR_2$-$C_6H_4$)-2-$PR'_2$-4,5-$Me_2$-1*H*-$C_3N_2$ (R = $C_6H_5$: R′ = $C_6H_5$, $^cC_6H_{11}$, $^cC_4H_3O$; R = $^cC_6H_{11}$: R′ = $C_6H_5$, $^cC_6H_{11}$, $^cC_4H_3O$) can be prepared in straightforward synthesis methodologies including Stelzer coupling[9] and selective metalation at position 2 of the imidazole unit. The diphosphino imidazoles gave upon their reaction with [$PdCl_2(SEt_2)_2$] palladamacrocycles of composition [Pd(1-(4-$PR_2$-$C_6H_4$)-2-$PR'_2$-4,5-$Me_2$-1*H*-$C_3N_2$)$Cl_2$]$_2$, which, however, are insoluble in common organic solvents. However, it appeared that the derivative with R = $C_6H_5$ and R′ = $^cC_4H_3O$ allowed the growth of single crystals suitable for X-ray structure analysis using the synthesis-*cum*-diffusion strategy. The structure of the latter molecule in the solid state shows the formation of a neutral 18-membered metal−organic cycle with two *trans*-configurated palladium centers. A further metallamacrocycle was accessible by treatment of [Pt(dppf)(C≡C-$C_6H_4$-4-$PPh_2$)$_2$] (dppf = 1,1′-bis(diphenylphosphino)-ferrocene), to enforce the required *cis*-geometry at the platinum atom, with [$Pt(SEt_2)_2Cl_2$] to give by molecular recognition [(Pt(dppf)(C≡C-$C_6H_4$-4-$PPh_2$))$PtCl_2$]$_2$. X-ray structure determination of this compound confirmed the molecular square architecture composed of Pt(dppf) and $PtCl_2$ corner units and 4-($C_6H_5$)$_2$P-$C_6H_4$-C≡C linkers. Similar compounds are known and well described.[6a,f,i,7] Furthermore, the mono- and bidentate phosphino imidazoles 1-(4-$PR_2$-$C_6H_4$)-4,5-$Me_2$-1*H*-$C_3N_2$ and 1-(4-$PR_2$-$C_6H_4$)-2-$PR'_2$-4,5-$Me_2$-1*H*-$C_3N_2$, respectively, were used in the palladium-catalyzed Suzuki cross-coupling of, for example, 2-bromotoluene with phenylboronic acid using potassium carbonate as base under aqueous reaction conditions.[14] All *in situ* generated phosphino palladium species showed moderate to high catalytic activity toward the formation of 2-methylbiphenyl. It was found that the monophosphine species were less active and productive than the catalysts based on diphosphines. The diphosphino systems featuring phenyl and cyclohexyl groups show a similar activity and productivity with conversions of 86−100%; the ones carrying weak σ-donating furyl groups show productivities comparable to the appropriate monophosphines. However, the best results were obtained with diphosphines carrying strong σ-donating substituents. In addition, we investigated the catalytic behavior of 1-(4-P($C_6H_5$)$_2$-$C_6H_4$)-4,5-$Me_2$-1*H*-$C_3N_2$ and 1-(4-P($^cC_6H_{11}$)$_2$-$C_6H_4$)-2-P($C_6H_5$)$_2$-4,5-$Me_2$-1*H*-$C_3N_2$ in the Suzuki coupling of 4-chlorotoluene with phenylboronic acid under non-aqueous conditions,[2b] in which especially the diphosphine showed excellent productivities, with TONs up to 8900. Furthermore, 1-(4-P($^cC_6H_{11}$)$_2$-$C_6H_4$)-2-P($C_6H_5$)$_2$-4,5-$Me_2$-1*H*-$C_3N_2$ was applied in the synthesis of *ortho*-substituted biaryls with a palladium loading of 0.05 mol % at 50 °C under non-aqueous conditions,[16] showing good to excellent conversions. Compared to other catalytically active species[2b,f,15,16] reported by Fu, Beller, and Buchwald, our systems show at least the same or higher productivities but at lower catalyst loadings and lower temperatures.

## EXPERIMENTAL SECTION

**General Procedures.** All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Tetrahydrofuran and dichloromethane were purified by distillation from sodium/benzophenone and calcium hydride, respectively; di-isopropylamine was purified by distillation from potassium hydroxide. Column chromatography was carried out using silica with a particle size of 40−60 μm (230−400 mesh (ASTM), Becker) or alumina with a particle size of 90 μm (standard, Merck KGaA). For filtrations Celite (purified and annealed, Erg. B.6, Riedel de Haen) was used.

NMR spectra were recorded at 298 K with a Bruker Avance 250 or a Bruker Avance III 500 spectrometer. The $^1$H NMR spectra were recorded at 250.13 or 500.3 MHz, the $^{13}C\{^1H\}$ at 125.7 MHz, and the $^{31}P\{^1H\}$ NMR spectra at 101.249 or 202.5 MHz, respectively. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as reference signal ($^1$H NMR: standard internal $CDCl_3$, δ 7.26; $^{13}C\{^1H\}$ NMR: standard internal $CDCl_3$, δ 77.16; $^{31}P\{^1H\}$ NMR: standard external rel 85% $H_3PO_4$, δ 0.0; $P(OMe)_3$, δ 139.0). High-resolution mass spectra were recorded with a Bruker Daltonik micrOTOF-QII spectrometer (ESI-TOF). ESI-TOF mass spectra of **11** were recorded on an Applied Biosystems spectrometer. Elemental analyses were carried out with a Thermo FlashAE 1112 series instrument. Melting points of analytically pure samples were determined by a Gallenkamp MFB 595 010 M melting point apparatus. FT IR spectra were recorded with a Thermo Nicolet IR 200 spectrometer using KBr pellets or NaCl plates. All starting materials were obtained from commercial suppliers and used without further purification. 1-(4-Iodophenyl)-4,5-dimethyl-1*H*-imidazole (**2**),[2f] borane-diphenylphosphine **3a**,[17] borane-dicyclohexylphosphine **3b**,[18] chlorophosphines **5b**[19] and **5c**,[19] [$PdCl_2(SEt_2)_2$],[20] [$PtCl_2$(dppf)],[21] and HC≡C-$C_6H_4$-4-P($C_6H_5$)$_2$[22] were prepared according to published procedures.

**Synthesis of 1-(4-(Diphenylphosphino)phenyl)-4,5-dimethyl-1*H*-imidazole (4a).** Compound **2** (0.50 g, 1.68 mmol), potassium acetate (0.20 g, 2.04 mmol, 1.2 equiv), and [$Pd(OAc)_2$] (3.8 mg, 1.0 mol %) were dissolved in dimethylacetamide (40 mL). Then borane-diphenylphosphine **3a** (0.34 g, 1.70 mmol) was added in a single portion, and the reaction mixture was stirred for 3 h at 130 °C. After cooling to ambient temperature, the reaction mixture was poured into water (50 mL) and extracted twice with dichloromethane (20 mL). The dichloromethane solution was then washed five times with water (30 mL) and dried over magnesium sulfate. The solvent was removed in a membrane-pump vacuum, and the crude product was purified by column chromatography on silica (column size: 3.5 × 15 cm) using a mixture of *n*-hexane−diethyl ether (ratio 1:1, v:v). Phosphine **4a** could be isolated as a colorless solid. Yield: 0.31 g (0.87 mmol, 52% based on **2**). Anal. Calcd for $C_{23}H_{21}N_2P$ (356.40 g/mol): C, 77.51; H, 6.23; N, 7.86. Found: C, 77.13; H, 5.97; N, 7.80. Mp: 162 °C. IR (KBr, ν/cm$^{-1}$): 1432 (m, P−C), 1500 (s, N=C), 1574/1594 (m, C=C), 2912/2942/2998 (w, C−H), 3052 (w, =C−H). $^1$H NMR (500.30 MHz, $CDCl_3$, δ): 2.11 (s, 3 H, $CH_3$), 2.22 (s, 3 H, $CH_3$), 7.22 (dpt, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 1.9 Hz, $^4J_{HP}$ = 1.1 Hz, 2 H, $H^m/C_6H_4$), 7.33−7.40 (m, 12 H, $H^{o,m,p}/C_6H_5$+$H^o/C_6H_4$), 7.50 (s, 1 H, $H^2/C_3HN_2$). $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$, δ): 8.9 (s, $CH_3$), 12.1 (s, $CH_3$), 122.6 (s, $C^{4,5}/C_3HN_2$), 125.0 (d, $^3J_{CP}$ = 6.7 Hz, $C^m/C_6H_4$), 128.4 (d, $^3J_{CP}$ = 7.1 Hz, $C^m/C_6H_5$), 128.8 (s, $C^p/C_6H_5$), 133.5 (d, $^2J_{CP}$ = 19.8 Hz, $C^o/C_6H_5$), 133.8 (s, $C^{4,5}/C_3HN_2$), 134.3 (d, $^2J_{CP}$ = 19.6 Hz, $C^o/C_6H_4$), 134.7 (s, $C^p/C_6H_4$), 136.2 (d, $^1J_{CP}$ = 10.9 Hz, $C^i/C_6H_5$), 136.6 (s, $C^2/C_3HN_2$), 137.8 (d, $^1J_{CP}$ = 13.7 Hz, $C^i/C_6H_4$). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, δ): −5.9 (s). HRMS (ESI-TOF) $C_{23}H_{21}N_2P$ [M + *n*H]$^+$ *m*/*z*: calcd 357.1515, found 357.1516; [M + *n*Na]$^+$ *m*/*z*: calcd 379.1335, found 379.1325; [2M + *n*Na]$^+$ *m*/*z*: calcd 735.2777, found 735.2815.

**Synthesis of 1-(4-(Dicyclohexylphosphino)phenyl)-4,5-dimethyl-1*H*-imidazole (4b).** To a dimethylacetamide solution (40 mL) containing **2** (0.50 g, 1.68 mmol), potassium acetate (0.20 g, 2.04 mmol, 1.2 equiv), and [$Pd(OAc)_2$] (3.8 mg, 1.0 mol %) was added borane-dicyclohexylphosphine **3b** (0.36 g, 1.70 mmol) in a single portion, and the reaction mixture was stirred for 3 h at 130 °C.


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Afterward, the reaction mixture was cooled to ambient temperature, poured into water (50 mL), and extracted twice with dichloromethane (20 mL). The dichloromethane solution was washed five times with water (30 mL) and dried over magnesium sulfate. After removal of all volatiles in a membrane-pump vacuum, the crude product was purified by column chromatography on silica (column size: 3.5 × 15 cm) using a mixture of *n*-hexane−diethyl ether (ratio 1:1, v:v). Phosphine **4b** could be isolated as a colorless solid. Yield: 0.30 g (0.81 mmol, 48% based on **2**). Anal. Calcd for $C_{23}H_{33}N_2P$ (368.50 g/mol): C, 74.97; H, 9.03; N, 7.60. Found: C, 74.46; H, 8.87; N, 7.52. Mp: 97 °C. IR (NaCl, $\nu$/cm$^{-1}$): 1447 (m, P−C), 1499 (s, N═C), 1595 (m, C═C), 2849/2932 (s, C−H), 3032 (w, ═C−H). $^1$H NMR (500.30 MHz, $CDCl_3$, $\delta$): 0.99−1.07 (m, 2 H, $C_6H_{11}$), 1.11−1.39 (m, 8 H, $C_6H_{11}$), 1.63−1.73 (m, 6 H, $C_6H_{11}$), 1.79−1.82 (m, 2 H, $C_6H_{11}$), 1.88−1.98 (m, 4 H, $C_6H_{11}$), 2.14 (s, 3 H, $CH_3$), 2.24 (s, 3 H, $CH_3$), 7.25 (dpt, $^3J_{HH}$ = 8.2 Hz, 2 H, $H^m/C_6H_4$), 7.52 (s, 1 H, $H^2/C_3HN_2$), 7.57−7.50 (m, 2 H, $H^o/C_6H_4$). $^{13}$C{$^1$H} NMR (125.81 MHz, $CDCl_3$, $\delta$): 9.3 (s, $CH_3$), 12.8 (s, $CH_3$), 26.4 (s, $C_6H_{11}$), 26.9 (d, $J_{CP}$ = 7.4 Hz, $C_6H_{11}$), 27.2 (d, $J_{CP}$ = 12.5 Hz, $C_6H_{11}$), 28.8 (d, $J_{CP}$ = 7.2 Hz, $C_6H_{11}$), 30.0 (d, $J_{CP}$ = 16.2 Hz, $C_6H_{11}$), 32.6 (d, $J_{CP}$ = 12.1 Hz, $C_6H_{11}$), 122.7 (s, $C^{4,5}/C_3HN_2$), 124.6 (d, $^3J_{CP}$ = 7.3 Hz, $C^m/C_6H_4$), 134.7 (s, $C^{4,5}/C_3HN_2$), 135.1 (d, $^2J_{CP}$ = 20.5 Hz, $C^o/C_6H_4$), 135.1 (s, $C^p/C_6H_4$), 135.6 (d, $^1J_{CP}$ = 19.6 Hz, $C^i/C_6H_4$), 137.3 (s, $C^2/C_3HN_2$). $^{31}$P{$^1$H} NMR (202.5 MHz, $CDCl_3$, $\delta$): 2.7 (s). HRMS (ESI-TOF) $C_{23}H_{33}N_2P$ $[M]^+$ *m*/*z*: calcd 369.2454, found 369.2447.

**General Synthesis Procedure for Phosphines 6a−f.** To 0.30 g of **4a** (0.84 mmol) or **4b** (0.81 mmol) dissolved in dry diethyl ether (40 mL) was added dropwise 1 equiv of a 2.0 M solution of lithium diisopropylamide at −30 °C. After warming the reaction mixture to ambient temperature, it was again cooled to −30 °C, and 1 equiv of the appropriate pure chlorophosphine (**5a−c**) was added dropwise. The reaction mixture was stirred at ambient temperature for 2 h, and the solvent was removed under vacuum. The crude product was purified by column chromatography on silica and dried under vacuum.

**Synthesis of 1-(4-(Diphenylphosphino)phenyl)-2-(diphenylphosphino)-4,5-dimethyl-1*H*-imidazole (6a).** Following the synthesis procedure described above, **4a** (0.30 g, 0.84 mmol) was reacted with lithium di-isopropylamide (0.42 mL, 0.84 mmol) and the chlorophosphine **5a** (0.15 mL, 0.84 mmol). The resulting residue was purified by column chromatography on silica (column size: 15 × 2.5 cm) using a mixture of *n*-hexane−diethyl ether (ratio 1:1, v:v) as eluent. Phosphine **6a** was obtained as a colorless solid. Yield: 0.26 g (0.48 mmol, 57% based on **4a**). Anal. Calcd for $C_{35}H_{30}N_2P_2$ (540.57 g/mol): C, 77.76; H, 5.59; N, 5.18. Found: C, 77.91; H, 5.76; N, 5.10. Mp: 96 °C. IR (KBr, $\nu$/cm$^{-1}$): 1435 (s, P−C), 1479/1498 (m, N═C), 1593 (w, C═C), 2863/2918/2966 (w, C−H), 3051 (w, ═C−H). $^1$H NMR (500.30 MHz, $CDCl_3$, $\delta$): 1.97 (s, 3 H, $CH_3$), 2.25 (s, 3 H, $CH_3$), 7.00 (dpt, $^3J_{HH}$ = 8.4 Hz, 2 H, $H^m/C_6H_4$), 7.25−7.28 (m, 8 H, $C_6H_5$), 7.32−7.38 (m, 10 H, $H^o/C_6H_4$ + $C_6H_5$), 7.40−7.45 (m, 4 H, $C_6H_5$). $^{13}$C{$^1$H} NMR (125.81 MHz, $CDCl_3$, $\delta$): 9.7 (s, $CH_3$), 13.2 (s, $CH_3$), 127.1 (s, $C^{4,5}/C_3N_2$), 128.2 (dd, $^3J_{CP}$ = 3.1 Hz, $^4J_{CP}$ = 2.8 Hz, $C^m/C_6H_4$), 128.4 (d, $^3J_{CP}$ = 7.4 Hz, $C^m/C_6H_5$), 128.7 (d, $^3J_{CP}$ = 4.2 Hz, $C^m/C_6H_5$), 128.8 (s, $C^p/C_6H_5$), 129.2 (s, $C^p/C_6H_5$), 133.8 (d, $^2J_{CP}$ = 20.7 Hz, $C^o/C_6H_5$), 134.0 (d, $^2J_{CP}$ = 19.7 Hz, $C^o/C_6H_5$), 134.1 (d, $^2J_{CP}$ = 19.6 Hz, $C^o/C_6H_4$), 136.3 (d, $^3J_{CP}$ = 6.2 Hz, $C^{4,5}/C_3N_2$), 136.5 (d, $^3J_{CP}$ = 1.9 Hz, $C^p/C_6H_4$), 136.7 (d, $^1J_{CP}$ = 10.9 Hz, $C^i/C_6H_5$), 137.5 (d, $^1J_{CP}$ = 1.9 Hz, $C^i/C_6H_5$), 138.5 (d, $^1J_{CP}$ = 13.0 Hz, $C^i/C_6H_4$), 144.0 (d, $^1J_{CP}$ = 1.9 Hz, $C^2/C_3N_2$). $^{31}$P{$^1$H} NMR (202.5 MHz, $CDCl_3$, $\delta$): −27.9 (s, {$C_3N_2PPh_2$}), −5.5 (s, {$C_6H_4PPh_2$}). HRMS (ESI-TOF) $C_{35}H_{30}N_2P_2$ $[M + nH]^+$ *m*/*z*: calcd 541.1957, found 541.1915.

**Synthesis of 1-(4-(Diphenylphosphino)phenyl)-2-(dicyclohexylphosphino)-4,5-dimethyl-1*H*-imidazole (6b).** As described earlier, **4a** (0.30 g, 0.84 mmol) was reacted with lithium di-isopropylamide (0.42 mL, 0.84 mmol) and chlorodicyclohexylphosphine (**5b**) (0.19 mL, 0.86 mmol). The crude product was purified by column chromatography on silica (column size: 15 × 2.5 cm) using a mixture of *n*-hexane−diethyl ether (ratio 2:1, v:v) as eluent. Phosphine **6b** was obtained as a colorless solid. Yield: 0.23 g (0.42 mmol, 50% based on **4a**). Anal. Calcd for $C_{35}H_{42}N_2P_2$ (552.67 g/mol): C, 76.06; H, 7.66; N, 5.07. Found: C, 75.79; H, 7.73; N, 4.93. Mp: 144 °C. IR (KBr, $\nu$/cm$^{-1}$): 1433 (m, P−C), 1497 (m, N═C), 1591 (w, C═C), 2847/2918 (s, C−H), 3046/3068 (w, ═C−H). $^1$H NMR (500.30 MHz, $CDCl_3$, $\delta$): 0.94−1.22 (m, 10 H, $C_6H_{11}$), 1.52−1.65 (m, 10 H, $C_6H_{11}$), 1.87 (s, 3 H, $CH_3$), 2.01−2.06 (m, 2 H, $H^1/C_6H_{11}$), 2.18 (s, 3 H, $CH_3$), 7.02 (dpt, $^3J_{HH}$ = 8.2 Hz, 2 H, $H^m/C_6H_4$), 7.25−7.29 (m, 12 H, $H^o/C_6H_4$ + $C_6H_5$). $^{13}$C{$^1$H} NMR (125.81 MHz, $CDCl_3$, $\delta$): 9.7 (s, $CH_3$), 13.0 (s, $CH_3$), 26.4 (s, $C_6H_{11}$), 26.8 (d, $J_{CP}$ = 8.3 Hz, $C_6H_{11}$), 26.9 (d, $J_{CP}$ = 11.8 Hz, $C_6H_{11}$), 29.4 (d, $J_{CP}$ = 7.8 Hz, $C_6H_{11}$), 30.4 (d, $J_{CP}$ = 17.0 Hz, $C_6H_{11}$), 34.3 (d, $^1J_{CP}$ = 8.0 Hz, $C^1/C_6H_{11}$), 125.3 (s, $C^{4,5}/C_3N_2$), 128.6 (d, $^3J_{CP}$ = 7.2 Hz, $C^m/C_6H_5$), 128.7 (dd, $^3J_{CP}$ = 3.1 Hz, $^4J_{CP}$ = 2.8 Hz, $C^m/C_6H_4$), 129.0 (s, $C^p/C_6H_5$), 133.7 (d, $^1J_{CP}$ = 19.5 Hz, $C^o/C_6H_4$), 133.9 (d, $^1J_{CP}$ = 19.9 Hz, $C^o/C_6H_5$), 135.5 (s, $C^{4,5}/C_3N_2$), 136.6 (d, $^1J_{CP}$ = 11.2 Hz, $C^i/C_6H_5$), 137.9 (d, $^1J_{CP}$ = 13.1 Hz, $C^i/C_6H_4$), 138.0 (d, $^3J_{CP}$ = 1.8 Hz, $C^p/C_6H_4$), 144.7 (d, $^1J_{CP}$ = 13.9 Hz, $C^2/C_3N_2$). $^{31}$P{$^1$H} NMR (202.5 MHz, $CDCl_3$, $\delta$): −23.1 (s, $P(C_6H_{11})_2$), −5.6 (s, $PPh_2$). HRMS (ESI-TOF) $C_{35}H_{42}N_2P_2$ $[M + nH]^+$ *m*/*z*: calcd 553.2825, found 553.2896.

**Synthesis of 1-(4-(Diphenylphosphino)phenyl)-2-(di-2-furylphosphino)-4,5-dimethyl-1*H*-imidazole (6c).** Molecule **4a** (0.30 g, 0.84 mmol) was reacted with lithium di-isopropylamide (0.42 mL, 0.84 mmol) and chlorodi-2-furylphosphine (**5c**) (0.17 g, 0.85 mmol) as described above. The residue was purified by column chromatography on silica (column size: 15 × 2.5 cm) using diethyl ether as eluent. Molecule **6c** was obtained as a colorless solid. Yield: 0.28 g (0.54 mmol, 64% based on **4a**). Anal. Calcd for $C_{31}H_{26}N_2O_2P_2$ (520.50 g/mol): C, 71.53; H, 5.03; N, 5.38. Found: C, 71.87; H, 5.19; N, 5.18. Mp: 65 °C. IR (NaCl, $\nu$/cm$^{-1}$): 1006 (s, C−O), 1434 (m, P−C), 1497 (m, N═C), 1592 (w, C═C), 2919 (w, C−H), 3051 (w, ═C−H). $^1$H NMR (500.30 MHz, $CDCl_3$, $\delta$): 1.94 (s, 3 H, $CH_3$), 2.25 (s, 3 H, $CH_3$), 6.31 (dt $^4J_{HP}$ = 1.6 Hz, $^3J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 1.8 Hz, 2 H, $H^4/C_4H_3O$), 6.71 (m, 2 H, $H^3/C_4H_3O$), 7.02 (m, $^3J_{HH}$ = 8.4 Hz, 2 H, $H^m/C_6H_4$), 7.30 (m, 2 H, $H^o/C_6H_4$), 7.35−7.40 (m, 10 H, $C_6H_5$), 7.59 (m, 2 H, $H^5/C_4H_3O$). $^{13}$C{$^1$H} NMR (125.81 MHz, $CDCl_3$, $\delta$): 9.5 (s, $CH_3$), 13.2 (s, $CH_3$), 110.9 (d, $^3J_{CP}$ = 6.6 Hz, $C^4/C_4H_3O$), 121.9 (d, $^2J_{CP}$ = 26.7 Hz, $C^3/C_4H_3O$), 127.5 (s, $C^4/C_3N_2$), 127.7 (dd, $^3J_{CP}$ = 2.5 Hz, $^4J_{CP}$ = 2.3 Hz, $C^m/C_6H_4$), 128.7 (d, $^3J_{CP}$ = 7.1 Hz, $C^m/C_6H_5$), 129.2 Hz, (s, $C^p/C_6H_5$), 133.9 (d, $^2J_{CP}$ = 19.9 Hz, $C^o/C_6H_4$), 134.1 (d, $^2J_{CP}$ = 19.8 Hz, $C^o/C_6H_5$), 136.4 (d, $^4J_{CP}$ = 3.8 Hz, $C^5/C_3N_2$), 136.6 (d, $^1J_{CP}$ = 10.9 Hz, $C^i/C_6H_5$), 137.2 (d, $^3J_{CP}$ = 1.2 Hz, $C^p/C_6H_4$), 138.7 (d, $^1J_{CP}$ = 13.6 Hz, $C^i/C_6H_4$), 140.4 (d, $^1J_{CP}$ = 12.5 Hz, $C^2/C_3N_2$), 147.6 (d, $^4J_{CP}$ = 2.6 Hz, $C^5/C_4H_3O$), 148.2 (d, $^1J_{CP}$ = 4.3 Hz, $C^2/C_4H_3O$). $^{31}$P{$^1$H} NMR (202.5 MHz, $CDCl_3$, $\delta$): −71.7 (s, $P(^cC_4H_3O)_2$), −5.6 (s, $PPh_2$). HRMS (ESI-TOF) $C_{31}H_{26}N_2O_2P_2$ $[M + nH]^+$ *m*/*z*: calcd 521.1542, found 521.1542.

**Synthesis of 1-(4-(Dicyclohexylphosphino)phenyl)-2-(diphenylphosphino)-4,5-dimethyl-1*H*-imidazole (6d).** Based on the general procedure described earlier, **4b** (0.30 g, 0.81 mmol) was reacted with lithium di-isopropylamide (0.41 mL, 0.82 mmol) and chlorodiphenylphosphine (**5a**) (0.15 mL, 0.84 mmol). The residue was purified by column chromatography on silica (column size: 15 × 2.5 cm) using a mixture of *n*-hexane−diethyl ether (ratio 2:1, v:v) as eluent. The product **6d** was obtained as a colorless solid. Yield: 0.27 g (0.49 mmol, 60% based on **4b**). Anal. Calcd for $C_{35}H_{42}N_2P_2$ (552.67 g/mol): C, 76.06; H, 7.66; N, 5.07. Found: C, 75.86; H, 7.62; N, 4.94. Mp: 155 °C. IR (NaCl, $\nu$/cm$^{-1}$): 1435 (m, P−C), 1497 (m, N═C), 1592 (w, C═C), 2849/2922 (s, C−H), 3051 (w, ═C−H). $^1$H NMR (500.30 MHz, $CDCl_3$, $\delta$): 1.08−1.18 (m, 2 H, $C_6H_{11}$), 1.23−1.37 (m, 8 H, $C_6H_{11}$), 1.59−1.73 (m, 6 H, $C_6H_{11}$), 1.79−1.92 (m, 6 H, $C_6H_{11}$), 1.97 (s, 3 H, $CH_3$), 2.25 (s, 3 H, $CH_3$), 6.98 (m, $^3J_{HH}$ = 7.9 Hz, 2 H, $H^m/C_6H_4$), 7.24−7.78 (m, 6 H, $H^{m,p}/C_6H_5$), 7.38−7.43 (m, 6 H, $H^o/C_6H_4$ + $H^o/C_6H_5$). $^{13}$C{$^1$H} NMR (125.81 MHz, $CDCl_3$, $\delta$): 9.7 (s, $CH_3$), 13.2 (s, $CH_3$), 26.6 (s, $C_6H_{11}$), 27.1 (d, $J_{CP}$ = 7.3 Hz, $C_6H_{11}$), 27.4 (d, $J_{CP}$ = 12.4 Hz, $C_6H_{11}$), 29.0 (d, $J_{CP}$ = 7.1 Hz, $C_6H_{11}$), 30.1 (d, $J_{CP}$ = 16.1 Hz, $C_6H_{11}$), 32.7 (d, $J_{CP}$ = 12.2 Hz, $C_6H_{11}$), 127.2 (s, $C^4/C_3N_2$), 127.7 (dd, $^3J_{CP}$ = 2.8 Hz, $^4J_{CP}$ = 2.7 Hz, $C^m/C_6H_4$), 128.4 (d, $^3J_{CP}$ = 7.6 Hz, $C^m/C_6H_5$), 128.8 (s, $C^p/C_6H_5$), 134.0 (d, $^2J_{CP}$ = 20.7 Hz, $C^o/C_6H_5$), 135.1 (d, $^1J_{CP}$ = 19.3 Hz, $C^i/C_6H_5$), 135.9 (d, $^2J_{CP}$ = 20.1 Hz, $C^o/C_6H_4$), 136.2 (d, $^1J_{CP}$ = 6.6 Hz, $C^i/C_6H_4$), 136.2 (d, $^3J_{CP}$ = 2.0 Hz, $C^5/C_3N_2$), 137.5 (d, $^3J_{CP}$ = 1.8 Hz, $C^p/C_6H_4$), 144.2 (d, $^1J_{CP}$ = 2.8 Hz, $C^2/C_3N_2$). $^{31}$P{$^1$H} NMR (202.5 MHz, $CDCl_3$, $\delta$): −26.7 (s,


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$PPh_2$), 2.6 (s, $P(C_6H_{11})_2$). HRMS (ESI-TOF) $C_{35}H_{42}N_2P_2$ $[M + nH]^+$ $m/z$: calcd 553.2883, found 553.2896.

**Synthesis of 1-(4-(Dicyclohexylphosphino)phenyl)-2-(dicyclohexylphosphino)-4,5-dimethyl-1*H*-imidazole (6e).** Using the general synthesis methodology described above, **4b** (0.30 g, 0.81 mmol) was reacted with lithium di-isopropylamide (0.41 mL, 0.82 mmol) and chlorodicyclohexylphosphine (**5b**) (0.18 mL, 0.82 mmol). The crude product was purified by column chromatography on silica (column size: 15 × 2.5 cm) using a mixture of *n*-hexane−diethyl ether (ratio 3:1, v:v) as eluent. Phosphine **6e** was obtained as a colorless solid. Yield: 0.21 g (0.37 mmol, 46% based on **4b**). Anal. Calcd for $C_{35}H_{54}N_2P_2$ (564.76 g/mol): C, 74.43; H, 9.64; N, 4.96. Found: C, 74.68; H, 9.37; N, 4.72. Mp: 66 °C. IR (NaCl, $\nu/cm^{-1}$): 1446 (m, P−C), 1497 (m, N═C), 1594 (w, C═C), 2849/2923 (s, C−H), 3031 (w, ═C−H). $^1H$ NMR (500.30 MHz, $CDCl_3$, $\delta$): 0.95−1.04 (m, 4 H, $C_6H_{11}$), 1.08−1.35 (m, 16 H, $C_6H_{11}$), 1.60−1.70 (m, 16 H, $C_6H_{11}$), 1.77−1.79 (m, 2 H, $C_6H_{11}$), 1.83−1.91 (m, 4 H, $C_6H_{11}$), 1.94 (s, 3 H, $CH_3$), 2.04−2.09 (m, 2 H, $C_6H_{11}$), 2.25 (s, 3 H, $CH_3$), 7.09 (m, $^3J_{HH}$ = 8.0 Hz, 2 H, $H^m/C_6H_4$), 7.51 (m, $^3J_{HH}$ = 8.2 Hz, $^3J_{HP}$ = 1.9 Hz, 2 H, $H^o/C_6H_4$). $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$, $\delta$): 9.8 (s, $CH_3$), 13.1 (s, $CH_3$), 26.5 (s, $C_6H_{11}$), 26.5 (s, $C_6H_{11}$), 26.9 (d, $J_{CP}$ = 8.7 Hz, $C_6H_{11}$), 27.0 (d, $J_{CP}$ = 12.1 Hz, $C_6H_{11}$), 27.1 (d, $J_{CP}$ = 6.8 Hz, $C_6H_{11}$), 27.3 (d, $J_{CP}$ = 12.4 Hz, $C_6H_{11}$), 29.0 (d, $J_{CP}$ = 7.4 Hz, $C_6H_{11}$), 29.7 (d, $J_{CP}$ = 8.1 Hz, $C_6H_{11}$), 30.1 (d, $J_{CP}$ = 16.2 Hz, $C_6H_{11}$), 30.5 (d, $J_{CP}$ = 16.9 Hz, $C_6H_{11}$), 32.7 (d, $J_{CP}$ = 12.3 Hz, $C_6H_{11}$), 34.2 (d, $J_{CP}$ = 8.4 Hz, $C_6H_{11}$), 125.8 (s, $C^4/C_3N_2$), 128.2 (dd, $^3J_{CP}$ = 7.2 Hz, $^4J_{CP}$ = 4.3 Hz, $C^m/C_6H_4$), 135.1 (d, $^2J_{CP}$ = 19.3 Hz, $C^o/C_6H_4$), 135.3 (d, $^1J_{CP}$ = 21.0 Hz, $C^i/C_6H_4$), 135.4 (s, $C^5/C_3N_2$), 138.1 (s, $C^p/C_6H_4$), 144.8 (d, $^1J_{CP}$ = 15.4 Hz, $C^2/C_3N_2$). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, $\delta$): −22.2 (s, $\{C_3N_2P(C_6H_{11})_2\}$), 2.6 (s, $\{C_6H_4P(C_6H_{11})_2\}$). HRMS (ESI-TOF) $C_{35}H_{54}N_2P_2$ $[M + nH]^+$ $m/z$: calcd 565.3871, found 565.3835.

**Synthesis of 1-(4-(Dicyclohexylphosphino)phenyl)-2-(di-2-furylphosphino)-4,5-dimethyl-1*H*-imidazole (6f).** Molecule **4b** (0.30 g, 0.81 mmol) was reacted with lithium di-isopropylamide (0.41 mL, 0.82 mmol) and chlorodi-2-furylphosphine (**5c**) (0.17 g, 0.85 mmol) as described earlier. The crude product was purified by column chromatography on silica (column size: 15 × 2.5 cm) using diethyl ether as eluent. Phosphine **6f** was obtained as a colorless solid. Yield: 0.28 g (0.53 mmol, 65% based on **4b**). Anal. Calcd for $C_{31}H_{38}N_2O_2P_2$ (532.59 g/mol): C, 69.91; H, 7.19; N, 5.26. Found: C, 70.15; H, 7.54; N, 4.95. Mp: 115 °C. IR (KBr, $\nu/cm^{-1}$): 1007 (m, C−O), 1449 (m, P−C), 1500/1507 (w, N═C), 1598 (w, C═C), 2854/2930 (s, C−H), 3122/3143 (w, ═C−H). $^1H$ NMR (500.30 MHz, $CDCl_3$, $\delta$): 0.93−1.05 (m, 2 H, $C_6H_{11}$), 1.07−1.17 (m, 4 H, $C_6H_{11}$), 1.20−1.37 (m, 6 H, $C_6H_{11}$), 1.57−1.72 (m, 6 H, $C_6H_{11}$), 1.78−1.87 (m, 4 H, $C_6H_{11}$), 1.90 (s, 3 H, $CH_3$), 2.21 (s, 3 H, $CH_3$), 6.28 (dt, $^4J_{HP}$ = 1.6 Hz, $^3J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 1.9 Hz, 2 H, $H^4/C_4H_3O$), 6.63 (m, 2 H, $H^3/C_4H_3O$), 6.98 (m, $^3J_{HH}$ = 8.0 Hz, 2 H, $H^m/C_6H_4$), 7.42 (m, $^3J_{HH}$ = 8.2 Hz, $^3J_{HP}$ = 1.9 Hz, 2 H, $H^o/C_6H_4$), 7.58 (m, 2 H, $H^5/C_4H_3O$). $^{13}C\{^1H\}$ NMR (125.81 MHz, $CDCl_3$, $\delta$): 9.6 (s, $CH_3$), 13.2 ($CH_3$), 26.0 (s, $C_6H_{11}$), 27.1 (d, $J_{CP}$ = 7.5 Hz, $C_6H_{11}$), 27.3 (d, $J_{CP}$ = 12.2 Hz, $C_6H_{11}$), 28.9 (d, $J_{CP}$ = 7.2 Hz, $C_6H_{11}$), 30.1 (d, $J_{CP}$ = 16.2 Hz, $C_6H_{11}$), 32.6 (d, $J_{CP}$ = 11.9 Hz, $C_6H_{11}$), 110.9 (d, $^3J_{CP}$ = 7.0 Hz, $C^4/C_4H_3O$), 122.1 (d, $^2J_{CP}$ = 27.5 Hz, $C^3/C_4H_3O$), 127.4 (s, $C^4/C_3N_2$), 127.6 (dd, $^3J_{CP}$ = 2.5 Hz, $^4J_{CP}$ = 2.3 Hz, $C^m/C_6H_4$), 135.3 (d, $^2J_{CP}$ = 19.6 Hz, $C^o/C_6H_4$), 136.6 (d, $^3J_{CP}$ = 4.2 Hz, $C^5/C_3N_2$), 137.2 (d, $^1J_{CP}$ = 14.9 Hz, $C^i/C_6H_4$), 139.7 (d, $^3J_{CP}$ = 1.7 Hz, $C^p/C_6H_4$), 140.4 (d, $^1J_{CP}$ = 11.7 Hz, $C^2/C_3N_2$), 147.7 (d, $^4J_{CP}$ = 2.5 Hz, $C^5/C_4H_3O$), 147.9 (d, $^1J_{CP}$ = 5.3 Hz, $C^2/C_4H_3O$). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, $\delta$): −70.8 (s, $P(^cC_4H_3O)_2$), 2.6 (s, $P(C_6H_{11})_2$). HRMS (ESI-TOF) $C_{31}H_{38}N_2O_2P_2$ $[M]^+$ $m/z$: calcd 549.2440, found 549.2430.

**Synthesis of [Pd(1-(4-P(C$_6$H$_5$)$_2$-C$_6$H$_4$)-2-P($^c$C$_4$H$_3$O)$_2$-4,5-Me$_2$-1*H*-C$_3$N$_2$)Cl$_2$]$_2$ (8).** Complex **8** was synthesized via the synthesis-*cum*-diffusion strategy to ensure the formation of crystals suitable for single-crystal X-ray structure analysis. Therefore, a solution of **6c** (20 mg, 0.04 mmol) in dichloromethane (2 mL) was inserted into a test tube and covered with a layer of dichloromethane (10 mL). Afterward, a solution of $[PdCl_2(SEt_2)_2]$ (**7**, 13 mg, 0.04 mmol) in dichloromethane (2 mL) was added slowly. The resulting yellow crystals were subjected to single-crystal X-ray structure analysis.

**Synthesis of [Pt(dppf)(C≡C-C$_6$H$_4$-4-P(C$_6$H$_5$)$_2$)$_2$] (11).** $[PtCl_2(dppf)]$ (**9**, 0.7 g, 0.87 mmol) was dissolved in a dichloromethane−di-isopropylamine mixture (100 mL, ratio 7:3, v:v), followed by the addition of [CuI] (5.7 mg, 0.1 mmol) and 2 equiv of **10** (0.5 g, 1.75 mmol). The reaction mixture was stirred for 6 h at ambient temperature and filtered through a pad of alumina. Afterward, the solvent was reduced under vacuum to 5 mL, and *n*-hexane (20 mL) was added. The supernatant layer was removed, and the precipitate was dissolved in dichloromethane (10 mL) and chromatographed on alumina (column size: 5 × 1.5 cm) using dichloromethane as eluent. After drying under vacuum, product **11** was obtained as a yellow solid. Yield: 495 mg (0.45 mmol, 51% based on **9**). Anal. Calcd for $C_{74}H_{56}FeP_4Pt$ (1320.05 g/mol): C, 67.33; H, 4.28. Found: C, 67.40; H, 4.50. Mp: 183 °C (dec). IR (KBr, $\nu/cm^{-1}$): 2114 (m, C≡C), 1432/1477 (s, P−C). $^1H$ NMR (250.13 MHz, $CDCl_3$, $\delta$): 4.18 (dpt, $^3J_{HH}$ = 1.8 Hz, $^3J_{HP}$ = 1.7 Hz, 4 H, $H^\alpha/C_5H_4$), 4.31 (pt, $^3J_{HH}$ = 1.8 Hz, 4 H, $C_5H_4$), 6.76 (dpt, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.7 Hz, $^3J_{HP}$ = 1.5 Hz, 4 H, $H^m/C_6H_4$), 6.91−6.95 (m, 4 H, $H^p/C_6H_5$), 7.20−7.24 (m, 8 H, $H^{o,m}/C_6H_5$), 7.28−7.30 (m, 20 H, $H^{o,m,p}/C_6H_5$), 7.35−7.38 (m, 4 H, $H^o/C_6H_4$), 7.80−7.84 (m, 8 H, $H^{o,m}/C_6H_5$). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, $\delta$): 72.9 (pt, $^2J_{PC}$ = 3.3 Hz, $C^\beta/C_5H_4$), 75.7 (pt, $^2J_{PC}$ = 5.0 Hz, $C^\alpha/C_5H_4$), 77.7 ($C^i/C_5H_4$*), 104.9 (d, $^2J_{CP}$ = 20.5 Hz, C≡C−P), 110.1 (d, $^1J_{CP}$ = 34.8 Hz, C≡C-P), 128.0 (pt, $^3J_{CP}$ = 5.3 Hz, $C^m/C_6H_5$(dppf)), 128.5 (d, $^3J_{CP}$ = 6.6 Hz, $C^m/C_6H_5$), 128.6 (s, $C^p/C_6H_5$), 128.9 (s, $C^p/C_6H_4$), 130.6 (s, $C^p/C_6H_5$(dppf)), 131.6 (d, $^3J_{CP}$ = 7.4 Hz, $C^m/C_6H_4$), 132.7 (d, $^2J_{CP}$ = 19.9 Hz, $C^o/C_6H_5$(dppf)), 132.8 (pt, $^1J_{CP}$ = 8.9 Hz, $C^i/C_6H_5$(dppf)), 133.4 (d, $^1J_{CP}$ = 5.1 Hz, $C^i/C_6H_4$), 133.8 (d, $^2J_{CP}$ = 19.5 Hz, $C^o/C_6H_4$), 135.0 (pt, $^2J_{CP}$ = 5.6 Hz, $C^o/C_6H_5$(dppf)), 137.9 (d, $^1J_{CP}$ = 10.8 Hz, $C^i/C_6H_5$). $^{31}P\{^1H\}$ NMR (101.249 MHz, $CDCl_3$, $\delta$): 6.6 ($P(C_6H_5)_2$), 13.5 ($^1J_{^{31}P-^{195}Pt}$ = 2374 Hz, dppf). MS (ESI-TOF) $C_{74}H_{56}FeP_4Pt$ $[M + H]^+$ $m/z$: calcd 1320.24, found 1320.6(45). *Signal concealed by $CDCl_3$.

**Synthesis of [Pt(dppf)(C≡C-C$_6$H$_4$-4-P(C$_6$H$_5$)$_2$)$_2$PtCl$_2$)]$_2$ (13).** To a solution of **11** (50 mg, 0.04 mmol) in dichloromethane (10 mL) was added $[PtCl_2(SEt_2)_2]$ (**12**, 14.2 mg, 0.04 mmol) in a single portion, and the reaction mixture was stirred for 1 h at ambient temperature. Afterward, the solvent was reduced under vacuum to 2 mL, and the formed complex was precipitated by addition of *n*-pentane (10 mL). The supernatant layer was decanted, and the yellow residue was washed twice with *n*-pentane (5 mL). After drying under vacuum, **13** was obtained as a yellow solid. Yield: 45 mg (0.014 mmol, 70% based on **12**). Anal. Calcd for $C_{148}H_{112}Cl_4Fe_2P_8Pt_4$ × 1/4 $CH_2Cl_2$ (3172.08 g/mol): C, 55.48; H, 3.54. Found: C, 55.20; H, 3.50. Mp: >247 °C (dec). IR (KBr, $\nu/cm^{-1}$): 2114 (s, C≡C), 1432/1481 (s, P−C). $^1H$ NMR (250.13 MHz, $CDCl_3$, $\delta$): 4.19 (pt, $^3J_{HH}$ = 2.0 Hz, 8 H, $C_5H_4$), 4.35 (pt, $^3J_{HH}$ = 2.0 Hz, 8 H, $C_5H_4$), 5.30 (s, $CH_2Cl_2$) 6.40−6.57 (m, 8 H, $H^m/C_6H_4$), 6.90−7.01 (m, 8 H, $H^p/C_6H_5$), 7.09−7.40 (m, 64 H, $C_6H_5$ + $H^o/C_6H_4$), 7.80−7.84 (m, 16 H, $H^{o,m}/C_6H_5$). $^{31}P\{^1H\}$ NMR (202.5, $CDCl_3$, $\delta$): 13.6 ($^1J_{^{31}P-^{195}Pt}$ = 3673.3 Hz, $P(C_6H_5)_2$), 14.7 ($^1J_{^{31}P-^{195}Pt}$ = 2380.1 Hz, dppf).

**General Procedure for the Suzuki Reaction (ref 14).** 2-Bromotoluene (500 mg, 2.92 mmol), phenylboronic acid (470 mg, 3.85 mmol, 1.3 equiv), potassium carbonate (1.21 g, 8.76 mmol, 3 equiv), and acetyl ferrocene (111 mg, 0.49 mmol) were dissolved in a 1,4-dioxane−water mixture (10 mL, ratio 2:1, v:v). After addition of 0.25 mol % of $[Pd(OAc)_2]$ and 0.5 mol % of the monophosphine (**4**) or 0.25 mol % of the appropriate diphosphine (**6**), the reaction mixture was stirred for 1 h at 100 °C. Samples of 1 mL were taken after 2.5, 5, 10, 20, 30, and 60 min and filtered through a pad of silica (column size: 6 × 2.5 cm) using diethyl ether as eluent. All volatiles were evaporated under reduced pressure, and the conversions were determined by $^1H$ NMR spectroscopy.

**General Procedure for the Suzuki Coupling of Aryl Chlorides (ref 2b).** 4-Chlorotoluene (379 mg, 3.0 mmol), phenylboronic acid (550 mg, 4.5 mmol, 1.5 equiv), potassium phosphate (1.27 g, 6.0 mmol, 3 equiv), and acetylferrocene (114 mg, 0.50 mmol) were dissolved in toluene (6 mL). After addition of 0.01 mol % $[Pd(OAc)_2]$ and 0.1 mol % of the appropriate monophosphine **4a** or 0.05 mol % of the diphosphine **6d**, the reaction mixture was stirred for 20 h at 100 °C. Afterward, a sample of 2 mL was taken and filtered


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through a pad of Celite. After evaporation of all volatiles under reduced pressure, the conversions were determined by $^1$H NMR spectroscopy.

**General Procedure for the Synthesis of Sterically Hindered Biaryls (ref 16).** Phenylboronic acid (183 mg, 1.5 mmol, 1.5 equiv), potassium phosphate (0.64 g, 3.0 mmol, 3.0 equiv), acetyl ferrocene (114 mg, 0.50 mmol), 0.05 mol % [$Pd_2(dba)_3$], and 0.05 mol % of **6d** were dissolved in toluene (2 mL). Afterward, the appropriate aryl bromide (1.0 mmol, 1.0 equiv) was added in a single portion, and the reaction mixture was stirred for 24 h at 50 °C. Thereafter, the reaction mixture was filtered through a pad of Celite, and the solvent was removed in a membrane-pump vacuum. The conversions were determined by $^1$H NMR spectroscopy.

**Crystal Structure Determination.** The crystal and intensity collection data for **8**, **11**, and **13** are summarized in Table S1 (Supporting Information). All data were collected on an Oxford Gemini S diffractometer with graphite-monochromatized Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) at 110 K (**8**) and graphite-monochromatized Cu K$\alpha$ radiation ($\lambda$ = 1.54184 Å) at 100 K (**11**, **13**). The structures were solved by direct methods using SHELXS-91[23] and refined by full-matrix least-squares procedures on $F^2$ using SHELXL-97.[24] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions.

## ■ ASSOCIATED CONTENT

### Supporting Information

CCDC 867788, CCDC 867790, and CCDC 867789 contain the supplementary crystallographic data for complexes **8**, **11**, and **13**. This material is available free of charge via the Internet at http://pubs.acs.org. These data can also be obtained free of charge from the Cambridge Crystallographic Database via www.ccdc.cam.ac.uk/products/csd/request/.

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### Notes

The authors declare no competing financial interest.

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