Direct Coupling of Oxazolines and N-Heterocyclic Carbenes: A Modular Approach to a New Class of C−N Donor Ligands for Homogeneous Catalysis

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Reaction of 1-mesityl imidazole with 2-bromo-4,4-dimethyloxazoline gave the 2-(4,4-dimethyl)oxazolinyl imidazolium salt **1**, which was converted to the silver N-heterocyclic carbene complex [Ag^{I}(carbene)Br] **2** by stirring **1** with Ag_2O in dichloromethane at room temperature. The crystal structure analysis confirmed the monomeric nature of complex **2**, the coordination around the metal being quasi-linear with a C(1)−Ag−Br bond angle of 169.4(1)° and a Ag−C(1) bond length of 2.093(4) Å. The silver complex **2** was reacted with [$PdCl_2$(COD)] to yield the corresponding mono-carbene-palladium complex **3**, for which an X-ray diffraction study established a distorted square planar configuration with the imidazolyl and the oxazolinyl ring lying in the molecular plane. The palladium complex **3** was found to be an active catalyst for the Heck and Suzuki C−C coupling reactions. The coupling of activated or deactivated bromoarenes proceeded rapidly even with a low catalyst loading (0.02 mol %), while the reaction with activated chloroarenes required a higher catalyst loading of 3 mol %.

Modular ligand design, based on the variation and recombination of larger structural subunits, is an efficient strategy in the development of novel molecular catalysts.[1] It allows the systematic geometric modeling of the active space in a catalytically active complex as well as the combination of donor functions possessing disparate coordination properties.[2] It is thus possible to combine strongly coordinating "anchor" functions with more labile ligating units which modulate the electronic properties of the metal center or impose a particular stereochemical environment in the ligand sphere of the central atom. Traditionally, phosphines have played the role of anchoring functions in ligand design in late transition metal chemistry.[3]

More recently, N-heterocyclic carbenes[4] have emerged as a new family of ligands for homogeneous catalysis which strongly coordinate to late transition metals.[5] Metal complexes bearing these ligands have been employed as catalysts in a large variety of chemical transformations. These include hydrosilylation,[6] ruthenium-catalyzed furane syntheses,[7] and olefin metathesis[8] or carbon monoxide−ethylene copolymerizations.[9] In addition, N-heterocyclic carbenes have been successfully applied in various palladium-catalyzed C−C coupling reactions,[10] in particular, the Heck and Suzuki reactions.[11]

While there is an ever growing number of ligand systems containing N-heterocyclic carbenes as pivotal ligating units,[12] the successful use of chiral versions of these ligands for asymmetric catalysis is still relatively rare. The use of monodentate chiral imidazoline-2-ylidene ligands **A** (Figure 1) derived from enantiomerically pure amine starting materials has been reported

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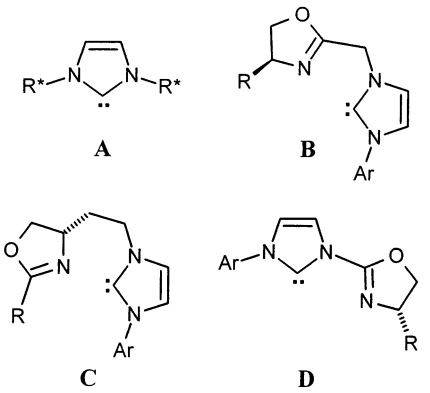


Figure 1. Examples of chiral N-heterocyclic carbene ligands.

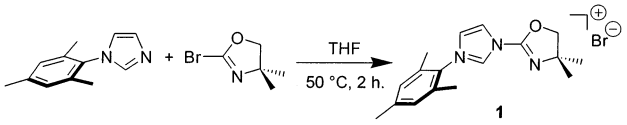
for various reactions, albeit with low to moderate enantiomeric excess.[13] An alternative to this approach is the combination of the carbene fragment with one of the established chiral donor functions of asymmetric catalysis.[14] Herrmann and co-workers reported the synthesis of several transition metal complexes coordinated by oxazolinylmethyl-N-heterocyclic carbenes **B**.[15] However, these compounds were apparently not successfully tested in catalytic reactions. More recently, Burgess et al. developed a new chelating chiral N-heterocyclic carbene **C**, which was successfully employed as a bidentate ligand in the catalytic hydrogenation of various olefins with enantiomeric excesses of up to 97%.[16]

In this paper we report the synthesis of a new type of oxazolinyl-carbene ligand, **D**, which is obtained by direct linkage of the two heterocycles, its palladium complex, and application of this compound in catalytic Heck and Suzuki type coupling reactions.[17] Our approach is based on the use of 2-bromooxazolines, which were found to act as versatile synthons in coupling reactions with a wide variety of nucleophilic reagents, enabling inter alia the access to a previously inaccessible class of oxazoline tripods.[18]

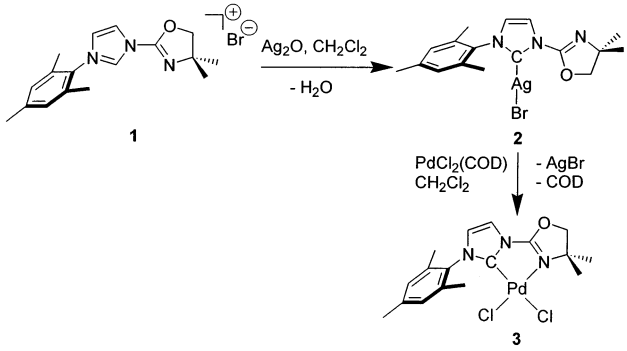
Results and Discussion

Synthesis of the Ligand Precursor and Its Coordination to Palladium(II). The coupling of the oxazoline unit and the imidazolium was carried out by adding 1-mesityl imidazole to a solution of 2-bromo-4,4-dimethyloxazoline in THF under nitrogen. Stirring at 50 °C led to the precipitation of the 2-(4,4-dimethyl)-oxazolinyl imidazolium salt **1** (Scheme 1) as a white solid, which was obtained after workup in about 80% yield.

Scheme 1. Synthesis of the Oxazolinyl-imidazolium Salt as a Ligand Precursor for the N-Heterocyclic Carbene



Scheme 2. Synthesis of the Silver Complex 2 and Its Use as a Ligand Transfer Reagent in the Preparation of the Palladium Complex 3



The complexation of **1** as an N-heterocyclic carbene ligand to palladium(II) proved not to be feasible by the standard synthetic routes, such as the direct metalation by reaction with $Pd(OAc)_2$ or the in situ deprotonation by an external base and reaction with a Pd^{II} source.[19] We therefore reverted to a strategy based on the use of a silver N-heterocyclic carbene complex as ligand transfer reagent for the synthesis of the desired palladium complex.[11c,20] Stirring **1** with Ag_2O in dichloromethane at room temperature for 3 h afforded the silver N-heterocyclic complex $[Ag^{I}(carbene)Br]$ **2** (Scheme 2). A high-resolution FAB mass spectrum was carried out in acetonitrile solution and displayed a molecular ion at 673.3, which corresponds to the silver bis(carbene) monocation, which suggests that a conversion of [Ag-(carbene)Br] to $[Ag(carbene)_2]^+$ occurs under the sampling conditions employed.[21] Furthermore the infrared spectroscopic data indicate that the oxazoline unit of the ligand is not bound to the metal center. The formation of the carbene complex was established by a signal at δ 186.2 ppm in the ^{13}C NMR spectrum which was assigned to the 2C-imidazol-2-ylidene carbon and by the absence of the resonance for the 2H-imidazolium proton

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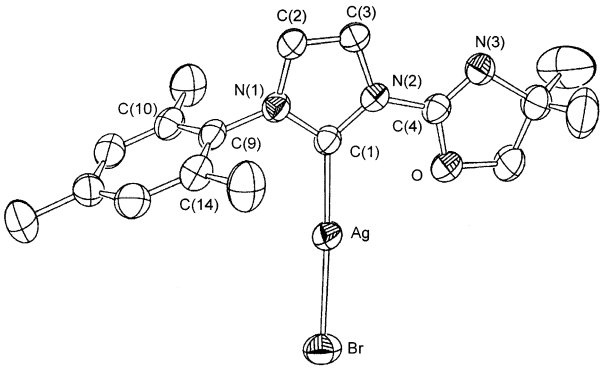


Figure 2. Molecular structure of **2**. Selected bond lengths (Å) and angles (deg): Ag−Br, 2.4303(6); Ag−C(1), 2.093(4); C(1)−N(1), 1.357(5); C(1)−N(2), 1.349(5); C(2)−C(3), 1.338(6); Br−Ag−C(1), 169.4(1).

in the ^{1}H NMR spectra. The details of the molecular structure of the silver carbene complex **2** in the solid state were established by a single-crystal X-ray diffraction study. The molecular structure of complex **2** is represented in Figure 2 along with the principal bond lengths and interbond angles.

The crystal structure analysis confirms the monomeric nature of complex **2**. The coordination around the metal is quasi-linear with a C(1)−Ag−Br bond angle of 169.4(1)° and a Ag−C(1) bond length of 2.093(4) Å, which is comparable with previously characterized examples of linear Ag(I)-NHC complexes.[21] The mesityl ring is oriented almost orthogonally to the imidazolyl ring [dihedral angle C(2)−N(1)−C(9)−C(10) 79°], while the oxazoline unit is arranged with the N atom pointing away from the metal center. The Ag-bonded imidazolyl ring and the adjacent oxazoline ring are only slightly twisted with respect to each other, the dihedral angle C(3)−N(2)−C(4)−N(3) being 5.1°. The Ag−O distance of 2.989 Å does not indicate a significant interaction with the silver atom.

The silver complex **2** was reacted with [$PdCl_2$(COD)] to yield the corresponding mono-carbene-palladium complex **3** in 69% yield (Scheme 2). The ^{1}H and ^{13}C NMR spectra are consistent with the formulation of **3** as a mononuclear complex, and the IR spectrum indicates that the oxazoline is coordinated to the Pd center (coordination shift of the ν(CN) band: 20 cm^{-1}). The molecular structure of complex **3** in the solid state was determined by X-ray diffraction and is depicted in Figure 3 along with the principal bond lengths and angles.

In complex **3** the palladium center adopts a distorted square planar conformation with the imidazolyl and the oxazolinyl ring lying in the molecular plane. As in the silver compound **2**, the mesityl ring plane is twisted almost orthogonally out of the plane of the central molecular unit [C(8)−N(3)−C(9)−C(14) 81.7°] while the two heterocycles of the bidentate ligand are essentially coplanar [C(8)−N(2)−C(3)−N(1) 1.1°]. The Pd(1)−Cl(2) bond length of 2.325(3) Å for the chloro ligand in the *trans* disposition to the carbene ligand is significantly longer than *trans* to the oxazoline-N donor atom [2.274(3) Å], which indicates the strong *trans* influence of the

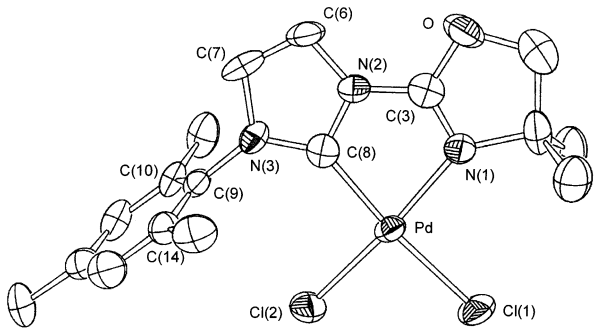
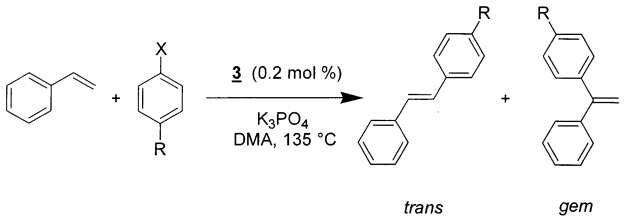


Figure 3. Molecular structure of **3**. Selected bond lengths (Å) and angles (deg): Pd(1)−Cl(1), 2.325(3); Pd(1)−Cl(2), 2.274(3); Pd(1)−N(1), 2.064(9); Pd(1)−C(8), 2.01(1); C(6)−C(7), 1.33(2); Cl(1)−Pd(1)−Cl(2), 90.7(1); Cl(1)−Pd(1)−N(1), 94.7(3); N(1)−Pd(1)−C(8), 79.2(4); Cl(2)−Pd(1)−C(8), 95.4(3).

Scheme 3. Pd-Catalyzed Heck Coupling Reaction between Styrene and Several Arylhalides Using 3 as a Molecular Catalyst



entry	X	R	reaction time (h)	GC conv. (%)	yield trans/gem[a]
1	Br	$COCH_3$	2	100	97/3
2	Br	CH_3	8	n.d.	74/6
3	Br	OMe	8	n.d.	68/7
4	Cl	$COCH_3$	18[b]	100	92/0[c]
5	Cl	NO_2	18[b]	100	89/0[c]

[a] ^{1}H NMR yield using di(ethyleneglycol)dibutyl ether as standard. [b] nBu_4Br (20 mol %) added to run. [c] isolated yield.

N-heterocyclic carbene ligand. This is consistent with previous structural studies on related complexes.[22]

Catalytic Heck and Suzuki Type C−C Coupling. Palladium complex **3** was found to be an active catalyst for the Heck reaction and proved to be thermally robust for high-temperature Heck olefination of aryl chlorides or bromides. The reaction between 4-chloroacetophenone and styrene was used as a test reaction for the optimization of the reaction conditions. The coupling proceeds in less than 18 h at 135 °C with K_3PO_4 as the base of choice. Use of other commonly employed bases for Heck type coupling reactions, such as K_2CO_3, NaOAc, Cs_2CO_3, or Hünig's base, led to a significant decrease of the yield. This catalytic system is able to couple activated aryl chlorides with styrene with a relatively low catalyst loading (entries 4 and 5 in Scheme 3) but is not suitable for nonactivated aryl chlorides even with a catalyst loading of 1 mol %. Interestingly, the selectivity of the catalyst differs upon going from aryl chlorides to the corresponding bromides.

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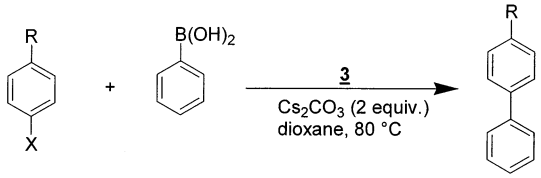
Scheme 4. Pd-Catalyzed Suzuki Coupling Reaction between Phenylboronic Acid and Several Arylhalides Using 3 as a Molecular Catalyst



entry	X	R	cat. loading (mol %)	time (h)	isolated yield (%)
1	Br	$COCH_3$	0.2	1.5	98
2	Br	OMe	0.2	1.5	92
3	Br	$COCH_3$	0.02	3	98
4	Br	OMe	0.02	3	94
5	Cl	$COCH_3$	3	1.5	74
6	Cl	NO_2	3	1.5	67
7	Cl	H	3	1.5	<5

Whereas the catalytic coupling of the activated aryl chlorides exclusively gave the *trans* stilbene derivatives, the use of the catalyst in the coupling of arylbromides gives a mixture of *trans* and *gem* stilbenes, the proportions of which depend on the para substituent (entries 1, 2, and 3 in Scheme 3). It is remarkable that the only minor component in the product mixture was found to be the geminally disubstituted alkene. The ^{1}H NMR chemical shift of its vinylic protons (δ 5.4−5.5) clearly distinguishes it from the vicinal *cis*-isomer (δ > 6.4).[23] In a first test of the activity of complex **3** in the Suzuki type coupling of para-substituted aryl halogenides with phenyl boronic acid, classical conditions for solvent and base were chosen (dioxane as solvent, Cs_2CO_3 as base, and reaction temperature of 80 °C).[10,24] The coupling of activated or deactivated bromoarenes and phenylboronic acid proceeds in high yields and quite rapidly even with a low catalyst loading of 0.02 mol % (entries 3, 4 in Scheme 4). Reactions with chloroarenes require a higher catalyst loading of 3 mol %. Under those conditions, 4-chloroacetophenone and 4-nitrochlorobenzene react very cleanly with phenylboronic acid in good yields (entries 5 and 6), while the conversion for the nonactivated chlorobenzene remains very low (entry 7).

Conclusions

The direct condensation of a 2-bromooxazoline derivative with an imidazole provides a facile modular route to a new family of C−N-donor ligands. The stability and catalytic activity of their palladium complexes is testimony to their potential in homogeneous catalysis of the late transition metals. Using chiral oxazolines, the strategy of ligand design is readily extended to chiral systems which may be employed in enantioselective transformations. This goal is currently being actively pursued in our laboratory.

Experimental Section

All manipulations were carried out under an inert atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were purified and dried by standard methods. 1-Mesitylimidazole,[25] 2-bromo-4,4-dimethyloxazoline,[26] and $[PdCl_2(COD)]$[27] were synthesized according to literature procedures. All other reagents were commercially available and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 and 75 MHz and were referenced using the residual proton solvent peak. Infrared spectra were obtained on a FT-IR Perkin-Elmer 1600. FAB mass spectra were recorded by the "service de spectrométrie de masse de l'Université Louis Pasteur" on an Autospec HF mass spectrometer. Elemental analyses were performed by the "service commun d'analyse élémentaire" of the Strasbourg Chemistry Department.

1-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-3-mesitylimidazolium Bromide (1). 1-Mesitylimidazole (1.11 g, 5.96 mmol) was added to a solution of 2-bromo-4,4-dimethyloxazoline (1.11 g, 6.23 mmol) in THF (ca. 1.0 M), and the mixture was heated at 50 °C for 2 h. A white solid precipitated during this time. After cooling, diethyl ether (10 mL) was added to complete precipitation. The product was filtered and washed with diethyl ether (2 × 10 mL) and dried in vacuo to yield 1.80 g (82%) of **1** as a white powder. ^{1}H NMR ($CDCl_3$): δ 10.57 (t, ^4J = 1.5 Hz, 1H, NC*H*N), 8.14 (dd, ^3J = 2.1 Hz, ^4J = 1.5 Hz, 1H, C$H_{4,5-\text{imidazolium}}$), 7.60 (dd, ^3J = 2.1 Hz, ^4J = 1.5 Hz, 1H, C$H_{4,5-\text{imidazolium}}$), 7.00 (s, 2H, C$H_{\text{mesityl}}$), 4.53 (s, 2H, C$H_2$), 2.32 (s, 3H, C$H_{3\text{para}}$), 2.16 (s, 6H, C$H_{3\text{ortho}}$), 1.45 (s, 6H, $CH_{3\text{oxazoline}}$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 148.8 (*C*NO), 142.2 (*C*$_{\text{mesityl}}$), 138.3 (N$_2$*C*), 134.4, 130.5 (*C*$_{\text{mesityl}}$), 130.4 (*C*H$_{\text{mesityl}}$), 125.8, 121.3 (*C*H$_{\text{imidazolium}}$), 83.2 (*C*H$_2$), 68.7 (*C*$_{4-\text{oxazoline}}$), 28.4 (*C*H$_{3\text{ortho}}$), 21.5 (*C*H$_{3\text{para}}$), 18.4 (*C*H$_{3\text{oxazoline}}$). MS (FAB) *m*/*z* (%): 284.0 (M)$^+$ (100), 187.0 (M − (C_5H_8NO))$^+$ (22). FT-IR (KBr): 1691 cm^{-1} (s, $\nu_{(C=N)}$). Anal. Calcd for $C_{17}H_{22}BrN_3O$: C, 56.05; H, 6.09; N, 11.54. Found: C, 55.66; H, 6.08; N, 11.49.

(1-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-3-mesitylimidazol-2-yl)silver(I) Bromide (2). The imidazolium **1** (1.15 g, 3.15 mmol) was dissolved in CH_2Cl_2 (40 mL), and silver(I) oxide (0.44 g, 1.90 mmol) was then added with exclusion of light. After 3 h stirring at room temperature, the mixture was centrifuged. The solution was then separated from the excess of silver(I) oxide and evaporated in vacuo. The obtained off-white solid was washed with diethyl ether (5 mL) and dried to yield **2** (1.37 g, 95%) as a white, light sensitive powder. Suitable crystals for X-ray diffraction were obtained by layering concentrated solutions of the compounds in dichloromethane with hexanes and allowing slow diffusion at room temperature. ^{1}H NMR (CD_2Cl_2): δ 7.79 (d, ^3J = 2.0 Hz, 1H, C$H_{4,5-\text{im.}}$), 7.06 (d, ^3J = 2.0 Hz, 1H, C$H_{4,5-\text{im.}}$), 7.01 (s, 2H, CH_{mesityl}), 4.35 (s, 2H, CH_2), 2.36 (s, 3H, C$H_{3\text{para}}$), 1.96 (s, 6H, C$H_{3\text{ortho}}$), 1.40 (s, 6H, C$H_{3\text{oxazoline}}$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 186.2 (N$_2$*C*), 152.6 (N*C*O), 140.3, 135.7, 134.9 (*C*$_{\text{mesityl}}$), 129.8 (*C*H$_{\text{mesityl}}$), 123.8, 120.6 (*C*H$_{\text{im.}}$), 82.0 (*C*H$_2$), 67.5 (*C*$_{4-\text{oxazoline}}$), 28.4 (*C*H$_{3\text{ortho}}$), 21.3 (*C*H$_{3\text{para}}$), 17.9 (*C*H$_{3\text{oxazoline}}$). MS (FAB) *m*/*z* (%): 673.0 (AgL_2)$^+$ (100), 390.0 (AgL)$^+$ (25), 284.0 (L)$^+$ (33). Anal. Calcd for $C_{17}H_{21}AgBrN_3O$: C, 43.34; H, 4.49; N, 8.92. Found: C, 43.82; H, 4.55; N, 8.86.

Dichloro-(1-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-mesitylimidazol-2-yl)palladium(II) (3). $PdCl_2$(1,5-COD) (275 mg, 0.96 mmol) was added to a solution of **2** (443 mg, 0.96 mmol) in CH_2Cl_2 with exclusion of light. The mixture became

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immediately cloudy. After 1.5 h at room temperature, the solution was filtered over Celite. The solvents were removed in vacuo, and the residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH, 97/3) to yield **3** (360 mg, 80%) as a yellow solid. Crystallization of **3** by slow evaporation of a chloroform solution gave yellow crystals suitable for an X-ray diffraction experiment. ^{1}H NMR ($CDCl_3$): δ 7.50 (d, ^3J = 2.2 Hz, 1H, C$H_{4,5-im.}$), 6.91 (s, 2H, C$H_{mesityl}$), 6.81 (d, ^3J = 2.2 Hz, 1H, C$H_{4,5-im.}$), 4.75 (s, 2H, CH_2), 2.30 (s, 3H, CH_{3para}), 2.07 (s, 6H, CH_{3ortho}), 1.77 (s, 6H, CH_{3oxa}). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 158.2, 157.0 ($C_{mesityl}$, NCO), 139.7, 133.9 ($C_{mesityl}$), 129.0 ($CH_{mesityl}$), 125.6, 116.8 ($CH_{im.}$), 87.1 (CH_2), 67.9 ($C_{4-oxazoline}$), 27.7 (CH_{3ortho}), 21.2 (CH_{3para}), 18.0 ($CH_{3oxazoline}$), the carbene ^{13}C NMR resonance was not observed. MS (FAB): *m*/*z* 426 ((PdClL)$^+$, 21), 388 ((PdL)$^+$, 26), 282 (L$^+$, 100), 185 (37). FT-IR (KBr): 1670 cm^{-1} (s, $\nu_{(C=N)}$). Anal. Calcd for $C_{17}H_{21}Cl_2N_3OPd$: C, 44.32; H, 4.59; N, 9.12. Found: C, 43.87; H, 4.66; N, 8.74.

General Procedure for the Heck Type Coupling Reactions. Catalyst (1.0 mg, 0.2 mol %), base (1.50 mmol), and Bu_4NBr (65 mg, 0.2 mmol) were placed in a Schlenk tube containing a small stirring bar. The Schlenk tube was conditioned, and styrene (230 μL, 2.0 mmol), di(ethylene glycol) dibutyl ether (124 μL, 0.50 mmol), DMA (2.5 mL), and the halogenoarene (1.0 mmol) were then added. The mixture was then heated. After the desired time, the conversion was determined either by ^{1}H NMR or by GC analysis. The mixture was diluted with Et_2O and filtered over a pad of silica. After evaporation of the solvents, the residue was purified by flash chromatography.

General Procedure for the Suzuki Type Coupling Reactions. Catalyst, Cs_2CO_3 (652 mg, 2 mmol), and phenylboronic acid (183 mg, 1.5 mmol) were added in a small Schlenk tube under nitrogen. Dioxane (3 mL) and the arylhalogenide (1 mmol) were then added, and the mixture was heated in an oil bath. At the conclusion of the reaction, the reaction mixture was cooled, diluted with Et_2O, filtered through a pad of silica gel with copious washings, concentrated, and purified by flash chromatography on silica gel (hexane/Et_2O).

X-ray Diffraction Study of 2 and 3. The crystal data were collected on a Nonius Kappa CCD diffractometer at −100 °C and transferred to a DEC Alpha workstation; for all subsequent calculations the Nonius OpenMoleN package was used.[28] The structures were solved using direct methods with absorption corrections being part of the scaling procedure of the data reductions. After refinement of the heavy atoms, difference Fourier maps revealed the maxima of residual electron density close to the positions expected for the hydrogen atoms; they were introduced as fixed contributors in the structure factor calculations with fixed coordinates (C−H: 0.95 Å) and isotropic temperature factors (B(H) = 1.3B_{eqv}(C) Å^2) but not refined. Full least-squares refinements on F^2 were performed. A final difference map revealed no significant maxima of electron density. The scattering factor coefficients and the anomalous dispersion coefficients were take from ref 29. Crystal data and experimental details for the crystals of **2** and **3** are given in Table 1.

Table 1. X-ray Experimental Data of Compounds 2 and 3

	2	**3**
formula	$C_{17}H_{21}AgBrN_3O$	$C_{17}H_{21}Cl_2N_3OPd\cdot 2CHCl_3$
molecular weight	471.16	699.44
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P12_11$
a (Å)	8.4139(3)	14.4233(4)
b (Å)	10.5463(4)	9.6890(2)
c (Å)	11.4073(6)	20.3978(6)
α (deg)	97.804(5)	
β (deg)	101.357(5)	90.360(5)
γ (deg)	102.576(5)	
V (Å^3)	951.57(7)	2850.5(1)
Z	2	4
ρ_{calc} (g cm^{-3})	1.64	1.63
F000	468	1392
μ (mm^{-1})	3.165	1.418
temperature (K)	294	173
wavelength (Å)	0.71073	0.71073
radiation	Mo Kα	Mo Kα
no. of data meas.	5531	13960
no. of data with $I > 3\sigma(I)$	3236	4006
no. of variables	208	576
R	0.044	0.042
wR_2	0.064	0.054
GOF	1.059	1.029

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Supporting Information Available: Text detailing the structure determination and tables of crystallographic data, the positional and thermal parameters, and interatomic distances and angles for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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