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Synthesis, Structural Studies, and Catalytic Application of Palladium Complexes Containing Anilido-Oxazolinate Ligands

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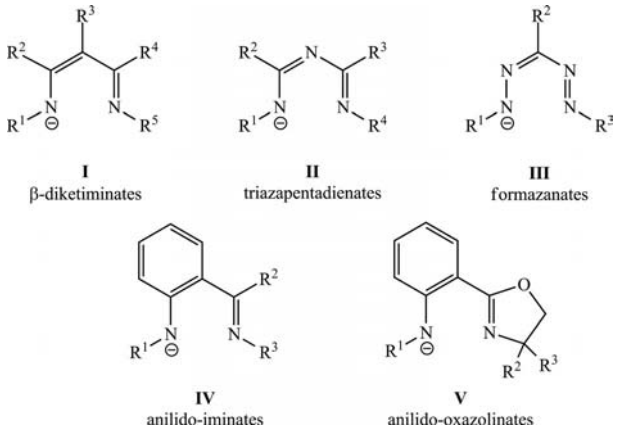
A series of palladium anilido-oxazolinate complexes **1**–**8** prepared from ligand precursors HNArOxa [*ortho*-C_6H_4(NHAr)-(4,4-dimethyl-2-oxazoline) where Ar = 2,4,6-trimethylphenyl, $HNPh^{TriMe}Oxa$; 2,6-diisopropylphenyl, $HNPh^{DiiPr}Oxa$; phenyl, $HNPh^{H}Oxa$; 2-methoxyphenyl, $HNPh^{OMe}Oxa$; 2-methylthiophenyl, $HNPh^{SMe}Oxa$] is reported. Treatment of HNArOxa with 1.1 equiv. $Pd(OAc)_2$ afforded palladium(II) acetate complexes ($NPh^{TriMe}Oxa$)Pd(η^2-OAc) (**1**) and ($NPh^{DiiPr}Oxa$)-Pd(η^2-OAc) (**2**) as monomeric complexes, [($NPh^{H}Oxa$)-Pd(OAc)]$_2$ (**3**) as an anilido-bridged dinuclear complex, [($NPh^{OMe}Oxa$)Pd(OAc)]$_2$ (**4**) as an acetate-bridged dinuclear complex, and ($NPh^{SMe}Oxa$)Pd(OAc) (**5**) as a monomeric complex. The reactions of **2**, **4**, and **5** with an excess of $NaCl_{(aq.)}$ in acetone yielded palladium(II) chloride complexes, [(NPh^{DiiPr}-Oxa)Pd(Cl)]$_2$ (**6**) as a chloro-bridged dinuclear complex, ($NPh^{OMe}Oxa$)Pd(Cl) (**7**) as a monomeric complex, [(NPh^{OMe}-Oxa)Pd(Cl)]$_2$ (**7′**) as an anilido-bridged dinuclear complex, and ($NPh^{SMe}Oxa$)Pd(Cl) (**8**) as a monomeric complex. The crystal and molecular structures of **1**–**8** are reported, and their application towards Suzuki and Heck reactions with a wide range of aryl halides has been examined.

Introduction

Monoanionic, nitrogen-based, bidentate ligands have attracted considerable attention in coordination and organometallic chemistry. Among these studies, β-diketiminates (Scheme 1, **I**) rapidly became benchmark ancillary ligands.[1a] Because of the relative ease of synthesis and the ability to tune the steric and electronic properties through the substitution of nitrogen or carbon atoms of the backbone, they work as ancillary ligands for a large number of main group and transition metals.[1] The impact of the ligand skeleton **I** is further demonstrated through the development of various ligand platforms, i.e. triazapentadienates (**II**),[2] formazanates (**III**),[3] and anilidoiminates (**IV**).[4] Anilido-oxazolinates (**V**), which originate from **IV** through the replacement of the imine group with the isoelectronic oxazolinate group, have received less attention.[5] Metal complexes bearing **I**–**V** as ancillary ligands have been studied and have demonstrated excellent catalytic activities in hydrogenation,[1c] hydrosilylation,[1d] hydroamination,[1e] cyclization,[1f] oxidation,[2l,4b] cross-coupling,[2f,5c–5e] cycloalkene oxide/CO_2 copolymerization,[1g,4c,5a] olefin polymerization,[1h–1l,3e,4d–4i] and ring-opening polymerization of cyclic esters.[1m–1o,4j–4m,5g–5i] Recently, some palladium complexes bearing **I**,[1j,1k,1u–1z] **II**,[2a–2g] **III**,[3b,3c] **IV**,[4a,4g] and **V**[5c–5f] have been synthesized and fully characterized. These ligands showed various bonding modes upon coordination to the palladium center. However, their catalytic activities have been less investigated.[1u–1z,2a–2e,2g,3b,3c,4a,5f] In our previous study, palladacycles bearing the pendant oxazolinate group exhibited better activities for Suzuki and Heck reactions than those with pendant pyridine or amine groups.[5d] Recently, zinc, aluminium, and magnesium complexes containing anilido-oxazolinate ligands have demonstrated efficient activities for the ring-opening polymerization of L-lactide and ε-caprolactone.[5g–5i] Therefore, palladium complexes bearing anilido-oxazolinate ligands, which are expected to have enhanced catalytic activities, have been explored. Due to the various bonding modes of the related bidentate ligands **I**–**IV**, structural studies of these new palladium complexes are reported. In order to investigate the



Scheme 1. β-Diketiminate **I** and analogues **II**–**V**.

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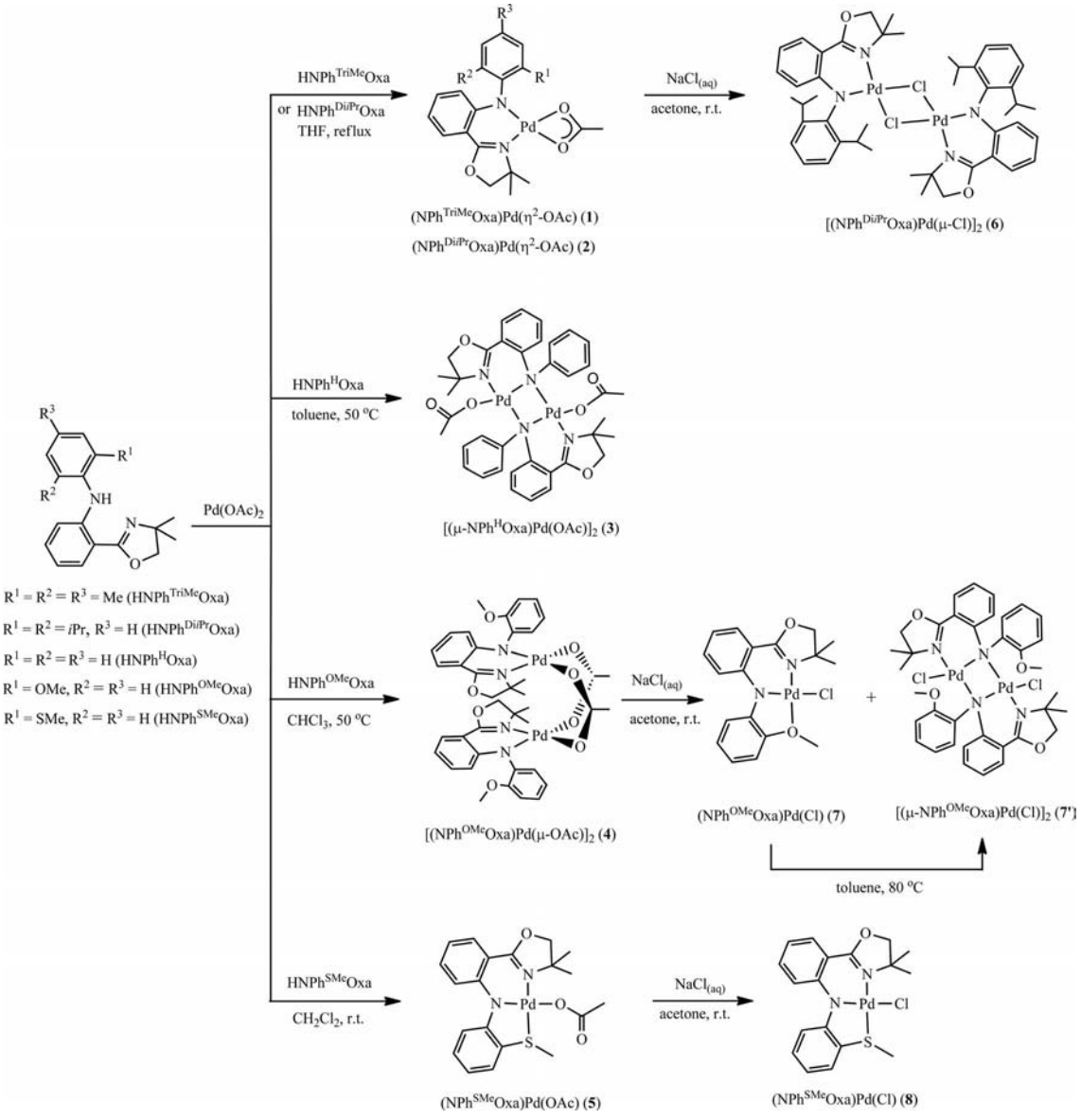
enhancement of catalytic activities caused by the introduction of the oxazolinate group, the catalytic application of **1**–**8** towards cross-coupling reactions has been examined.

Results and Discussion

Synthesis and Characterization of Acetate-Containing Palladium Complexes 1–5

Ligand precursors $HNPh^{TriMe}Oxa$, $HNPh^{Di\textit{i}Pr}Oxa$, $HNPh^{H}Oxa$, $HNPh^{OMe}Oxa$, and $HNPh^{SMe}Oxa$ were prepared as described previously.[5g,5h] Treatment of $HNPh^{TriMe}Oxa$ and $HNPh^{Di\textit{i}Pr}Oxa$ with $Pd(OAc)_2$ in hot tetrahydrofuran (THF) afforded **1** and **2** as dark green solids, respectively. Reaction of $HNPh^{H}Oxa$ with $Pd(OAc)_2$ in toluene at 50 °C yielded **3** as an orange solid. Treatment of $HNPh^{OMe}Oxa$ with $Pd(OAc)_2$ in $CHCl_3$ at 60 °C afforded **4** as a purple solid. Reaction of $HNPh^{SMe}Oxa$ with $Pd(OAc)_2$ in CH_2Cl_2 at room temperature afforded **5** as a purple solid. The synthesis and proposed structures of **1**–**5** are shown in Scheme 2. With the exception of **3**, these complexes were characterized by single-crystal X-ray diffraction, NMR spectroscopy, and elemental analysis. The disappearance of the N–H signal of the ligand precursors and the appearance of the resonance for protons of the acetate groups (1.74 for **1**, 1.70 for **2**, 1.26 for **4**, and 1.99 ppm for **5**) in the up-field region are consistent with the formation of palladium anilido-oxazolinate acetate complexes. Based on the molecular structures and NMR spectroscopic studies, the chemical shifts of the acetate groups were used as a reference for the different bonding modes (η^2-OAc for **1** and **2**, μ-OAc for **4**, and η^1-OAc for **5**). Because of its poor solubility in organic solvents, **3** was characterized by single-crystal X-ray diffraction, elemental analysis, and MS.



Scheme 2. Synthesis of palladium anilido-oxazolinate complexes **1**–**8**.

Suitable crystals for the structural determination of **1** and **2** were obtained from concentrated *n*-hexane solutions. The molecular structures of **1** and **2** are shown in Figures 1 and 2. The summation of the bond angles (359.91° for **1** and 360° for **2**) around Pd in each compound indicates a slightly distorted square-planar geometry, in which the Pd center is coordinated to two nitrogen atoms from the chelating anilido-oxazolinate ligand and two oxygen atoms from the η^2-acetate group. Unlike most acetate-bridged dinuclear palladium complexes, **1** and **2** are mononuclear complexes with a η^2-acetate ligand. This might result from the steric hindrance of the substituents on the anilido groups.[1k,1w] The $Pd–N_{oxazoline}$ [1.972(2) for **1**, 1.974(2) Å for **2**] and $Pd–N_{anilido}$ bonds [1.9578(19) for **1**, 1.9675(19) Å for **2**] are shorter than those found in structurally related palladium anilido-oxazolinate complexes [$Pd–N_{oxazoline}$ 2.0254(14)–2.0731(13) Å; $Pd–N_{anilido}$ 1.9942(13)–2.0077(14) Å][5c,5f] and close to those found in palladium β-diketiminate complexes [Pd–N 1.958(4)–2.1113(7) Å][1j,1k,1u–1z] and palladium anilidoiminate complexes [$Pd–N_{imine}$ 1.931–2.086(2) Å; $Pd–N_{anilido}$ 1.938(3)–2.109(3) Å].[6] The $N_{oxazoline}–Pd–N_{anilido}$ bite angles [90.55(8)° for **1**, 90.17(7)° for **2**] are close to those found in palladium anilido-oxazolinate complexes [$N_{oxazoline}–Pd–N_{anilido}$ 88.70(5)–90.01(6)°],[5c,5f] palladium anilidoiminate complexes [$N_{imine}–Pd–N_{anilido}$ 82.4(4)–93.1°],[6] and palladium β-diketiminate complexes [N–Pd–N 87.4(1)–93.74(8)°].[1j,1k,1u–1z] The $Pd–C_{acetate}$ distances [2.434 for **1**; 2.434 Å for **2**] are shorter than those found in palladium complexes containing η^2-acetate groups [$Pd–C_{acetate}$ 2.461(5)–2.509(5) Å].[1k,1w,7] The $Pd–O_{acteate}$ bond lengths [2.0814(17) and 2.0957(17) for **1**, 2.0830(18) and 2.0941(16) Å for **2**] and $O_{acetate}–Pd–O_{acetate}$ bite angles [62.41(7)° for **1**, 62.61(7)° for **2**] are close to those found in palladium complexes containing η^2-acetate groups [$Pd–O_{acteate}$ 2.089(4)–2.2591(14) Å; $O_{acetate}–Pd–O_{acetate}$ 59.92(14)–62.141(15)°].[1k,1w,7] Although most of the six-membered chelate rings of palladium β-diketiminate complexes adopt a half-chair or boat conformation,[1u,1v,1x,1y] the chelate rings of the palladium anilido-oxazolinate complexes are planar as evidenced by the dihedral angles between the planes defined by N(1)–Pd–N(2)/C(1)–C(6)–C(16), which is 6.3° for **1**, and N(1)–Pd–N(2)/C(1)–C(6)–C(19), which is 1.6° for **2**, and this conformation is consistent with other palladium β-diketiminate complexes.[1k,1u]

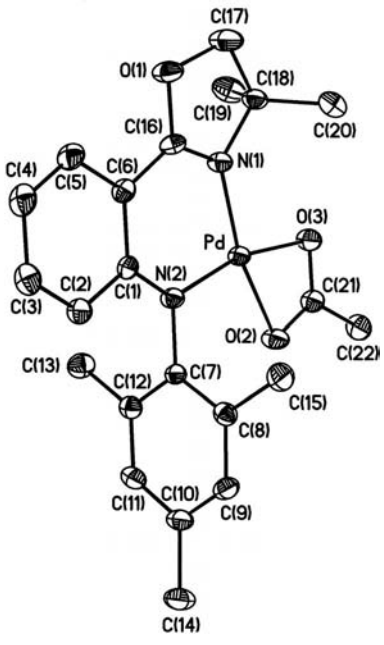


Figure 1. Molecular structure of **1**. Selected bond lengths [Å] and angles (°): Pd–N(1) 1.972(2); Pd–N(2) 1.9578(19); Pd–O(2) 2.0814(17); Pd–O(3) 2.0957(17); Pd···C(21) 2.434; N(1)–Pd–N(2) 90.55(8); O(2)–Pd–O(3) 62.41(7); N(1)–Pd–O(3) 104.84(8); N(2)–Pd–O(2) 102.19(8); N(1)–Pd–O(2) 167.10(8); N(2)–Pd–O(3) 164.60(8); O(2)–C(21)–O(3) 118.1(2); Pd–O(2)–C(21) 90.13(15). Hydrogen atoms on carbon atoms are omitted for clarity.

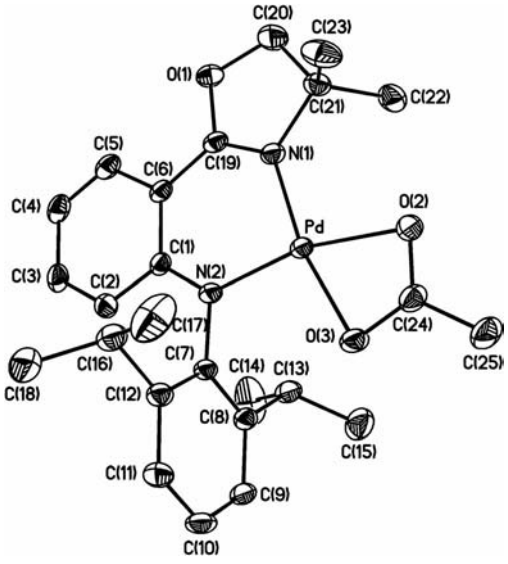


Figure 2. Molecular structure of **2**. Selected bond lengths [Å] and angles (°): Pd–N(1) 1.974(2); Pd–N(2) 1.9675(19); Pd–O(2) 2.0941(16); Pd–O(3) 2.0830(18); Pd···C(24) 2.434; N(1)–Pd–N(2) 90.17(7); O(2)–Pd–O(3) 62.61(7); N(1)–Pd–O(2) 105.29(7); N(2)–Pd–O(3) 101.93(6); N(1)–Pd–O(3) 167.90(8); N(2)–Pd–O(2) 164.51(6); O(2)–C(24)–O(3) 118.2(2); Pd–O(2)–C(24) 89.42(14). Hydrogen atoms on carbon atoms are omitted for clarity.

Suitable crystals for the structural determination of **3** were obtained from a toluene/*n*-hexane solution at room temperature. The molecular structure of **3** is depicted in Figure 3. Although several anilido-bridged palladium complexes (type **VI**) have been reported,[8] as shown in Scheme 3, examples of a bridged donor atom linked to terminal ligand (type **VII**) are relatively rare.[9] Based on its molecular structure, **3** is a type-**VII** palladium complex, in which each palladium center is coordinated to three nitrogen atoms (two from the same anilido-oxazolinate ligand and one from the second anilido-oxazolinate ligand) and one oxygen atom from η^1-acetate. The $Pd–N_{oxazoline}$ [Pd–N(1) 2.034(2) Å] and Pd–OAc bond lengths [Pd–O(2) 2.0328(16) Å] are similar to those discussed above. The $Pd–N_{anilido}$ bond lengths [Pd–N(2) 2.068(2) and Pd–N(2A) 2.0494(19) Å] are between type **VI** [2.047(2)–2.148(6) Å]

and type **VII** [2.037(2)–2.054(2) Å] complexes. The $N_{oxazoline}$–Pd–$N_{anilido}$ bite angles [N(1)–Pd–N(2A) 87.42(8)°] are smaller than those discussed above. This might result from the twist of the ligand backbone to fit the square-planar geometry. The distance between the two palladium centers [Pd···PdA 3.0419(4) Å] is between the range of type **VI** [3.0554(4)–3.1099(4) Å] and type **VII** [2.875 Å] complexes. Unlike **1** and **2**, the distorted six-membered chelate ring of **3** is characterized by the dihedral angle N(1)–Pd–N(2A)/C(1)–C(6)–C(14) of 43.3°.

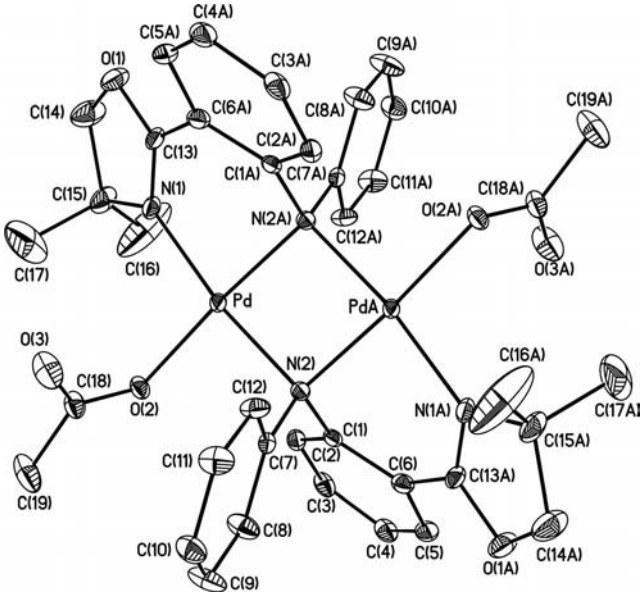
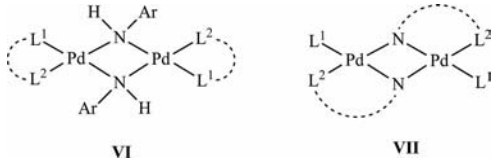


Figure 3. Molecular structure of **3**. Selected bond lengths [Å] and angles (°): Pd–N(1) 2.034(2); Pd–N(2) 2.068(2); Pd–N(2A) 2.0494(19); Pd–O(2) 2.0328(16); Pd···PdA, 3.0419(4); N(1)–Pd–N(2A) 87.42(8); N(2)–Pd–N(2A) 84.75(8); N(1)–Pd–N(2) 172.16(8); N(2A)–Pd–O(2) 175.96(7); Pd–N(2)–PdA, 95.25(8). Hydrogen atoms on carbon atoms are omitted for clarity.



Scheme 3. The classes of anilido-bridged dinuclear palladium complexes.

Suitable crystals for the structural determination of **4** were obtained from a concentrated CH_2Cl_2/*n*-hexane solution. The molecular structure of **4** is depicted in Figure 4. Because of the less bulky substituent on the anilido group than that of **1** and **2**, **4** is a dinuclear species with two bridging acetate ligands. Each palladium ion adopts as a slightly distorted square-planar geometry with two nitrogen atoms from the chelating anilido-oxazolinate ligand and two oxygen atoms from the bridging acetate ligands. As mentioned above, only one signal corresponding to the acetate ligand is observed in the ^1H NMR spectrum, which indicates an *anti* configuration[10a,10b] consistent with the solid state structure. The overall dimeric structure is similar to those found in the literature.[1w,1x,10] The Pd–$N_{oxazoline}$ [Pd–N(1) 2.0004(18) Å] and Pd–$N_{anilido}$ bond lengths [Pd–N(2) 1.9855(17) Å] and the $N_{oxazoline}$–Pd–$N_{anilido}$ bite angle [N(1)–Pd–N(2) 89.84(7)°] are close to those discussed above for palladium β-diketiminate complexes.[1j,1k,1u–1z] The Pd–$O_{acetate}$ bond lengths [Pd–O(2) 2.0649(15) Å and Pd–O(3) 2.0668(15) Å] are slightly longer than those found in dinuclear acetate-bridged palladium β-diketiminate complexes [Pd–$O_{acetate}$ 2.042(2)–2.062(2) Å].[1w,1x] Based on the van der Waals radii, there is no bond between the palladium ion and the oxygen atom from the methoxy group [Pd···O(4) 3.287 Å] in the solid state. The $O_{acetate}$–Pd–$O_{acetate}$ bond angle [O(2)–Pd–O(3) 85.63(6)°] is close to those found in dinuclear acetate-bridged palladium β-diketiminate complexes [$O_{acetate}$–Pd–$O_{acetate}$ 85.7(1)–88.39(9)°].[1w,1x] Similar to **3**, the distorted six-membered chelate ring of **4** is characterized by the dihedral angle N(1)–Pd–N(2)/C(1)–C(6)–C(14) of 35.6°.

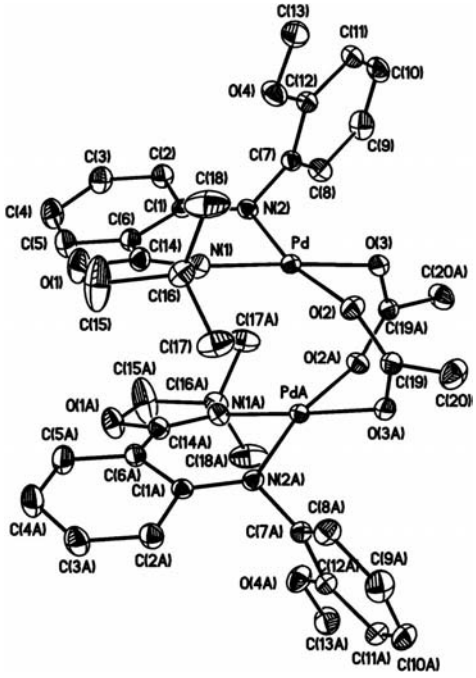


Figure 4. Molecular structure of **4**. Selected bond lengths [Å] and angles (°): Pd–N(1) 2.0004(18), Pd–N(2) 1.9855(17), Pd–O(2) 2.0649(15), Pd–O(3) 2.0668(15), Pd···PdA 3.0138(4), N(1)–Pd–N(2) 89.84(7), O(2)–Pd–O(3) 85.63(6), N(2)–Pd–O(3) 89.23(7), N(1)–Pd–O(2) 95.82(7), N(1)–Pd–O(3) 176.78(7), N(2)–Pd–O(2) 168.56(7), O(2)–C(19)–O(3A) 127.02(19), Pd–O(2)–C(19) 126.28(14). Hydrogen atoms on carbon atoms are omitted for clarity.

Suitable crystals for the structural determination of **5** were obtained from a CH_2Cl_2/*n*-hexane solution, and the molecular structure is shown in Figure 5. As discussed above, palladium complexes bearing anilido-oxazolinate ligands prefer to form a square-planar geometry with the stabilization of η^2-OAc or bridged-OAc groups. Therefore, the introduction of a side arm containing a soft donor atom would lead to the formation of more stable four-coordinate

complexes. Complex **5** demonstrates a distorted square-planar geometry, in which the palladium center is coordinated to two nitrogen atoms and one sulfur atom from the pendant anilido-oxazolinate ligand and one oxygen atom from a η^1-acetate group to form a mononuclear species. The Pd–$N_{oxazoline}$ [Pd–N(1) 2.055(4) Å] and Pd–$N_{anilido}$ bond lengths [Pd–N(2) 1.997(4) Å] and the $N_{oxazoline}$–Pd–$N_{anilido}$ bite angle [N(1)–Pd–N(2) 89.72(18)°] is similar to those discussed above. The Pd–$S_{thiomethyl}$ bond [Pd–S 2.2718(15) Å] is longer than those found in [*N*,*N*,*S*]-type palladium anilidoiminate complexes [Pd–S 2.2433(7)–2.2503(23) Å].[4g] The $N_{anilido}$–Pd–$S_{thiomethyl}$ bite angle [N(2)–Pd–S 85.27(14)°] is smaller than those found in palladium anilidoiminate complexes [85.61(10)–86.49(6)°].[4g] Similar to **4**, the distorted six-membered chelate ring of **5** is characterized by a dihedral angle N(1)–Pd–N(2)/C(1)–C(6)–C(14) of 35.6°.

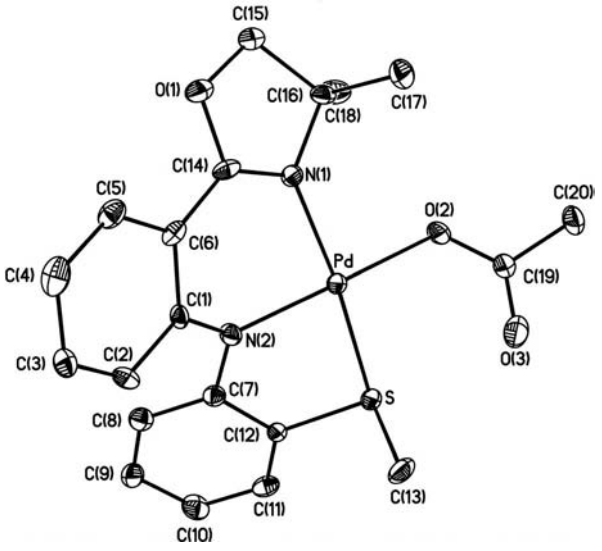


Figure 5. Molecular structure of **5**. Selected bond lengths [Å] and angles [°]: Pd–N(1) 2.055(4), Pd–N(2) 1.997(4), Pd–O(2) 2.021(4), Pd–S 2.2718(15), N(1)–Pd–N(2) 89.72(18), O(2)–Pd–S 93.98(14), N(1)–Pd–O(2) 90.9(2), N(2)–Pd–S 85.27(14), N(1)–Pd–S 174.22(14), N(2)–Pd–O(2) 176.7(2). Hydrogen atoms on carbon atoms are omitted for clarity.

Suitable crystals for the structural determination of **6** were obtained from a CH_2Cl_2/*n*-hexane solution, and the molecular structure of **6** is shown in Figure 6. Similar to palladium β-diketiminate chloride complexes,[1x] **6** demonstrates a chloro-bridged dinuclear species, in which each palladium center is coordinated to two nitrogen atoms from the chelating anilido-oxazolinate ligand and two bridging chloride ions. The Pd–$N_{oxazoline}$ [Pd–N(1) 2.0139(18) Å] and Pd–$N_{anilido}$ bond lengths [Pd–N(2) 1.9995(19) Å] and the $N_{oxazoline}$–Pd–$N_{anilido}$ bite angle [N(1)–Pd–N(2) 91.11(7)°] are close to those discussed above. The Pd–Cl bond lengths [Pd–Cl 2.3355(7) and 2.3334(7) Å] are close to those found in the corresponding palladium β-diketiminate chloride complex [2.342(1) and 2.356(1) Å].[1x] Similar to **1** and **2**, the chelate ring of **6** is planar as evidenced by the dihedral angle of 2.4° between the planes defined by N(1)–Pd–N(2)/C(1)–C(6)–C(19).

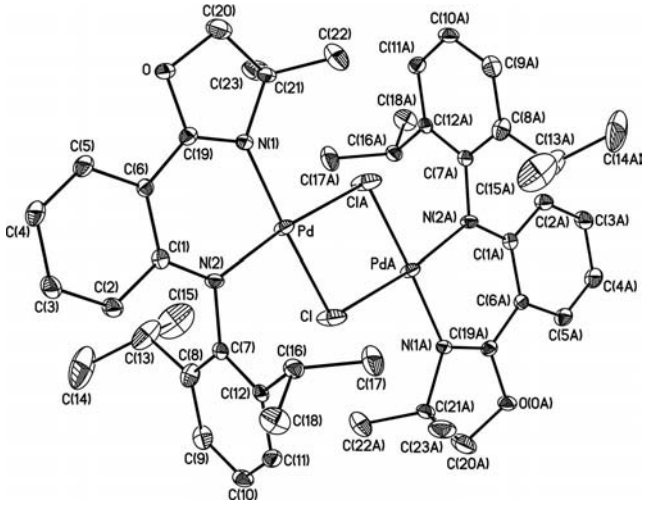


Figure 6. Molecular structure of **6**. Selected bond lengths [Å] and angles [°]: Pd–N(1) 2.0139(18), Pd–N(2) 1.9995(19), Pd–Cl 2.3355(7), Pd–ClA 2.3334(7), Pd···PdA 3.599, N(1)–Pd–N(2) 91.11(7), Cl–Pd–ClA 79.13(3), N(1)–Pd–ClA 96.35(3), N(2)–Pd–Cl 93.44(6), N(1)–Pd–Cl 174.99(5), N(2)–Pd–ClA 172.52(6), Pd–Cl–PdA 100.87(3). Hydrogen atoms on carbon atoms are omitted for clarity.

Synthesis and Characterization of Chloride-Containing Palladium Complexes 6–8

The reactions of **2**, **4**, and **5** with an excess of brine in acetone at room temperature yielded **6**, **7**, and **8**, respectively, as palladium chloride complexes. The synthesis and proposed structures of these complexes are shown in Scheme 2. Attempts to synthesize a palladium chloride complex from **1** using a similar route proved unsuccessful. Purification could not be achieved because of the similar solubility of the major product and byproduct. Compounds **6**–**8** were characterized by single-crystal X-ray diffraction, NMR spectroscopy, and elemental analysis. The disappearance of the acetate signal of the palladium acetate precursors in the NMR spectra was consistent with the formation of palladium chloride complexes.

Suitable crystals for the structural determination of **7** were obtained from a CH_2Cl_2/*n*-hexane solution, and the molecular structure of **7** is depicted in Figure 7. The pendant anilido-oxazolinate ligand is a tridentate ligand. Complex **7** demonstrates a distorted square-planar geometry, in which the palladium center is coordinated to two nitrogen atoms and one oxygen atom from the pendant anilido-oxazolinate ligand and one chloride ion to form a mononuclear species. The Pd–$N_{oxazoline}$ [Pd–N(1) 1.990(4) Å] and Pd–$N_{anilido}$ bond lengths [Pd–N(2) 1.979(4) Å] and the $N_{oxazoline}$–Pd–$N_{anilido}$ bite angle [N(1)–Pd–N(2) 90.01(16)°] are similar to those discussed above. The Pd–Cl bond length [Pd–Cl 2.3173(3) Å] is close to that found in another mononuclear palladium chloride complex [2.3158(8) Å].[10f] The Pd–$O_{methoxy}$ bond [Pd–O(2) 2.073(3) Å] is shorter than

those found in other palladium complexes bearing a pendant methoxy group [Pd–O 2.187(3)–2.4464(17) Å].[10f,11] The distorted six-membered chelate ring of **7** is characterized by a dihedral angle N(1)–Pd–N(2)/C(1)–C(6)–C(14) of 39.4°.

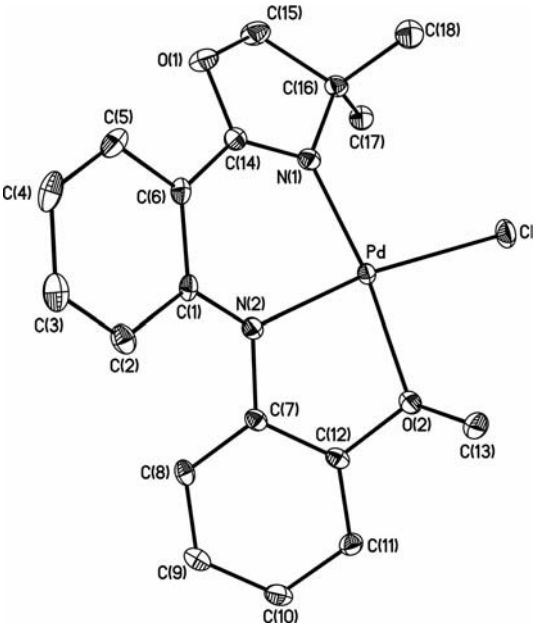


Figure 7. Molecular structure of **7**. Selected bond lengths [Å] and angles [°]: Pd–N(1) 1.990(4), Pd–N(2) 1.979(4), Pd–Cl 2.3173(12), Pd–O(2) 2.074(3), N(1)–Pd–N(2) 90.01(16), O(2)–Pd–Cl 88.51(10), N(1)–Pd–Cl 99.16(15), N(2)–Pd–O(2) 82.34(15), N(1)–Pd–O(2) 172.29(15), N(2)–Pd–Cl 170.80(12). Hydrogen atoms on carbon atoms are omitted for clarity.

A small amount of orange crystals were found during the recrystallization of **7** from a CH_2Cl_2/*n*-hexane solution at room temperature over a few days. Compound **7′** was also synthesized by allowing the solution of **7** in CH_2Cl_2/*n*-hexane to stand or by stirring the solution of **7** in $CHCl_3$ or toluene at room temperature for a few days. An alternative route for the preparation of **7′** by heating a solution of **7** in toluene at 80 °C for 2.5 days results in the formation of anilido-bridged palladium complexes as orange solids. Because of the poor solubility of **7′** in organic solvents, the ^{1}H NMR spectrum was only recorded in $CDCl_3$. Compound **7′** was also characterized by single-crystal X-ray diffraction and elemental analysis. The molecular structure of **7′** is depicted in Figure 8. Similar to **3**, **7′** is a type **VII** palladium complex, in which each palladium center is coordinated to three nitrogen atoms (two from the same anilido-oxazolinate ligand and one from the second anilido-oxazolinate ligand) and one chloride ion. The Pd–$N_{oxazoline}$ [Pd–N(1) 2.0285(16) Å], Pd–Cl [Pd–Cl 2.3326(5) Å], and Pd–$N_{anilido}$ bond lengths [Pd–N(2) 2.0918(15) and Pd–N(2A) 2.1007(14) Å] are similar to those discussed above. The $N_{oxazoline}$–Pd–$N_{anilido}$ bite angle [N(1)–Pd–N(2A) 85.84(6)°] is smaller than those discussed above, which might result from the twist of the ligand backbone to fit the square-planar geometry. The distance between two Pd centers [Pd···PdA 3.0252(2) Å] is similar to that in **3**. The distorted six-membered chelate ring of **7′** is characterized by the dihedral angle N(1)–Pd–N(2A)/C(1A)–C(6A)–C(14) of 60.9°.

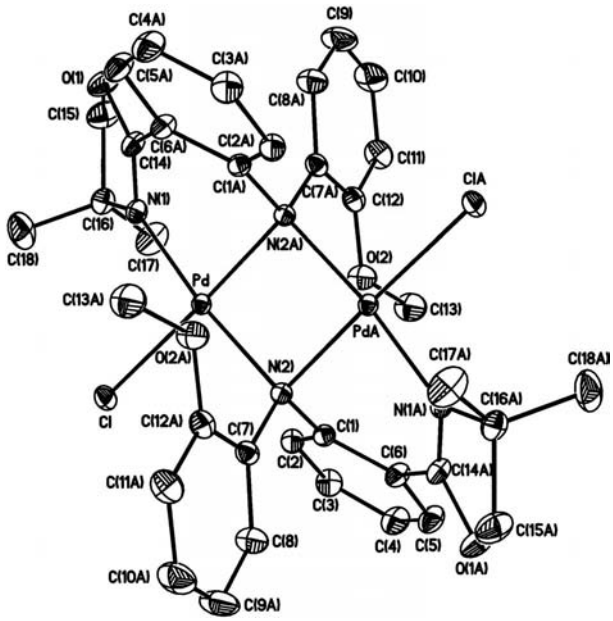


Figure 8. Molecular structure of **7′**. Selected bond lengths [Å] and angles [°]: Pd–N(1) 2.0285(16), Pd–N(2) 2.0918(15), Pd–N(2A) 2.1007(14), Pd–Cl 2.3326(5), Pd···PdA 3.0252(3), Pd···O(2) 2.928, N(1)–Pd–N(2A) 85.84(6), N(2)–Pd–N(2A) 87.63(6), N(1)–Pd–Cl 93.98(5), N(2)–Pd–Cl 92.59(4), N(1)–Pd–N(2) 173.43(6), N(2A)–Pd–Cl 174.08(4), Pd–N(2)–PdA 92.37(6). Hydrogen atoms on carbon atoms are omitted for clarity.

Two sets of signals were observed in the ^{1}H NMR spectra of **8** with relative intensities of 1.33:1 in C_6D_6, 1.22:1 in C_7D_8, and 1.86:1 in $CDCl_3$. $^{13}C\{^1H\}$ NMR spectroscopic studies confirmed these results. Attempts to separate these palladium chloride complexes by recrystallization or chromatography proved unsuccessful. Therefore, we propose that **8** consists of two isomers with different ligand coordination.[12] It is likely that the dynamic process is associated with versatile ligand bonding modes[12a,12b] or the fluxionality of the methyl group on the thioether functionality.[12c,12d] In order to gain more insight into this process, high temperature ^{1}H NMR studies were carried out for **8** in C_7D_8 from 293 K to 363 K. At 293 K, three kinds of signals could be clearly observed from the following: (1) the signals of the methyl group on the oxazoline group (H_a) are located in the range of 1.56–1.60 ppm, (2) two signals of the thiomethyl group (H_b) are located at 2.02 and 2.40 ppm with a ratio of relative intensities of 1.22:1, and (3) the signals of the methylene groups on the oxazoline group (H_c) are located at 3.35 and 3.66 ppm (overlap of two doublets). These peaks coalesced to broad signals upon heating from 323 to 343 K and merge to three broad peaks upon heating from 353 K to 363 K, as shown in Figure 9. These observations indicate that a dynamic process could occur in solution with different ligand coordination or fluxionality of the

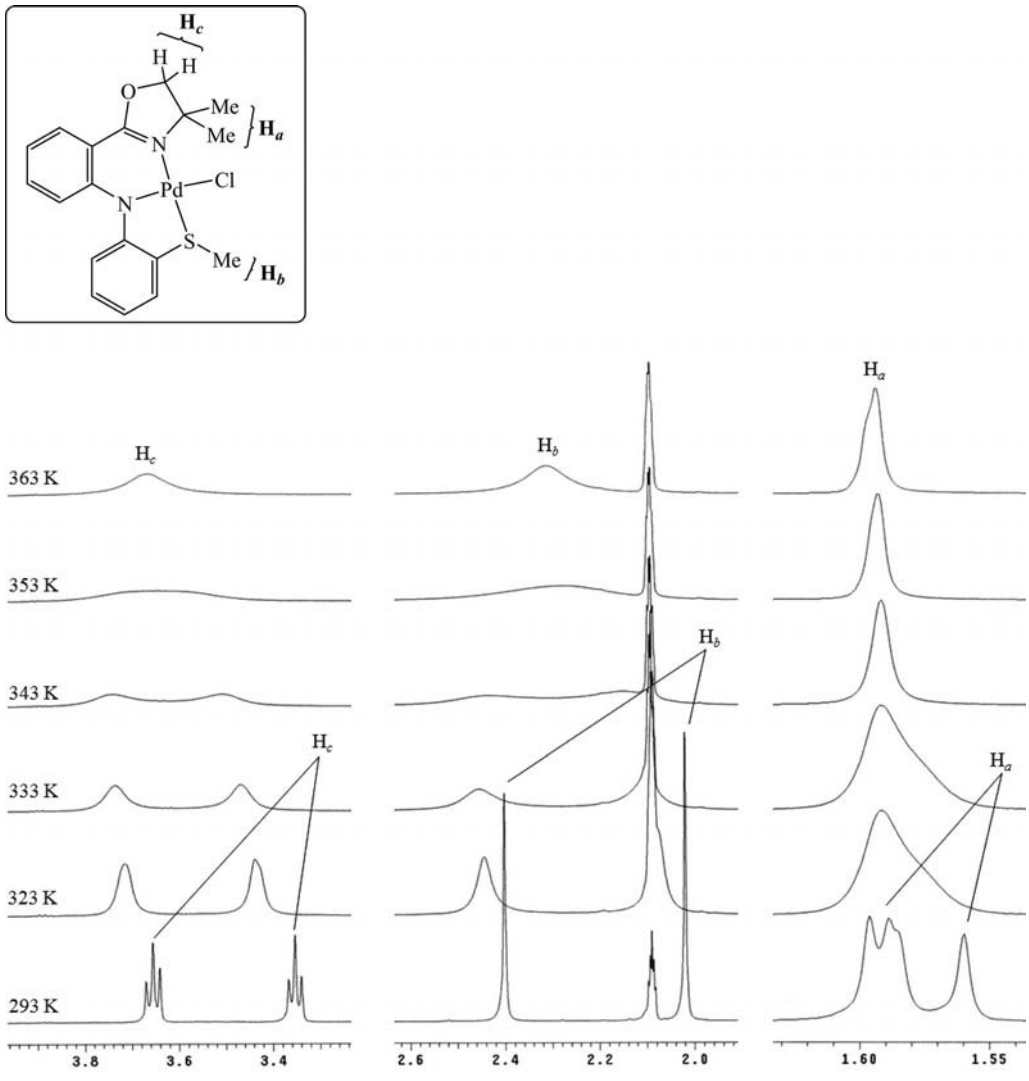


Figure 9. Variable temperature ^{1}H NMR spectra for **8** ([D_8]toluene, 600 MHz).

methyl group on the thioether functionality to form another chemical environment could occur, which supports the observation that such a ligand could coordinate to palladium by versatile bonding modes or different orientations and two conformers are found at room temperature. One of these two isomers was identified by single-crystal X-ray structure determination. Suitable crystals of **8** were obtained from a CH_2Cl_2/*n*-hexane solution, and the molecular structure of **8** is depicted in Figure 10. Complex **8** is similar to **5** but with a coordinated chloride ion instead of an acetate group. The bond lengths [Pd–$N_{oxazoline}$ 2.0490(18) Å; Pd–$N_{anilido}$ 2.0152(17) Å; Pd–S 2.2479(5) Å] and bite angle [$N_{oxazoline}$–Pd–$N_{anilido}$ 89.01(7)°] are similar to those discussed above for **5**. The Pd–Cl bond length [Pd–Cl 2.3234(6) Å] is close to that discussed above for **7**. Similar to **5**, The distorted six-membered chelate ring of **8** is characterized by the dihedral angle N(1)–Pd–N(2)/C(1)–C(6)–C(14) of 41.3°.

Catalytic Studies

Palladium-catalyzed cross-coupling reactions are powerful and convenient tools for carbon–carbon bond formation in modern organic synthesis.[13] Based on the catalytic cycles mentioned by most reports,[13] ancillary ligands with bulky, electron-rich properties, such as phosphanes[14] and N-heterocyclic carbenes,[15] play an important role in enhancing catalytic activity. However, sensitivity, toxicity, and economic considerations result in significant limitations on their synthetic application. Therefore, many metal complexes bearing nitrogen- or oxygen-based ligands,[16] such as guanidines,[16a] amidines,[16b,16c] diamines,[16d,16e] diimines,[16f–16i] simple amines,[16j,16k] Schiff bases (half SALEN),[16l–16r] and diketones,[16s] and heterocyclic ligands,[17] such as oxazolines,[5c,5d,17c–17h] pyridines,[17i–17l] quinolines,[17m] pyrazoles,[17n–17r] imidazoles,[17s–17u] 1,4-diazabicyclooctane,[17v–17x] and piperazines,[17y,17z] have been

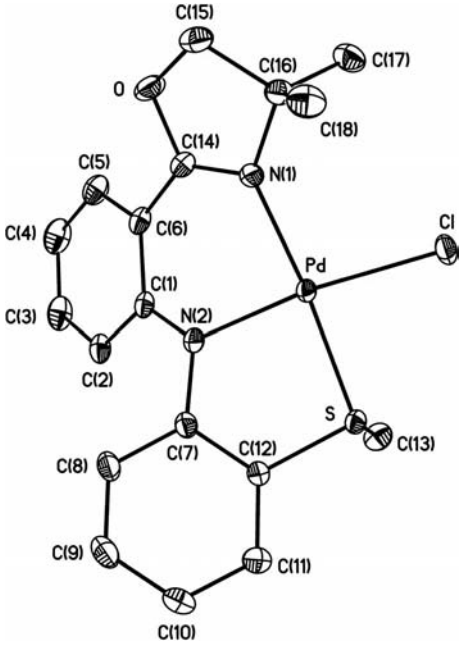
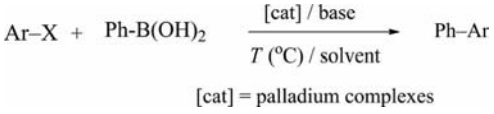


Figure 10. Molecular structure of **8**. Selected bond lengths [Å] and angles [°]: Pd–N(1) 2.0490(18), Pd–N(2) 2.0152(17), Pd–Cl 2.3234(6), Pd–S 2.2479(5), N(1)–Pd–N(2) 89.01(7), S–Pd–Cl 85.97(2), N(1)–Pd–Cl 98.37(5), N(2)–Pd–S 86.71(5), N(1)–Pd–S 175.03(5), N(2)–Pd–Cl 172.53(5). Hydrogen atoms on carbon atoms are omitted for clarity.

examined for their catalytic activities in cross-coupling reactions. Due to the success of some palladium complexes containing anilido or oxazoline groups in cross-coupling reactions, **1**–**8** are expected to work as catalysts in Suzuki and Heck reactions.

Suzuki Reaction

We examined the catalytic activities of **1**–**8** in the Suzuki reaction using the coupling of aryl halides with phenylbronic acid on a 1 mol-% Pd scale, as shown in Scheme 4. Selected results are listed in Table 1. The solvent system was optimized by introducing nonpolar or polar solvents, such as toluene, THF, dichloromethane, acetonitrile, *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), methanol or H_2O, in the coupling of 4-bromoanisole with phenylboronic acid in the presence of K_3PO_4 at room temperature on a 1 mol-% scale with **2**. However, poor conversions (< 30%) were observed within 30 min (Entries 1–8). The catalytic activity was improved by using a biphasic system in the presence of TBAB (tetra-*n*-butylammonium bromide).[18] Complex **2** was used to examine the catalytic activities on a 1 mol-% scale using 4-bromoanisole as the substrate with the volume ratio of solvent/H_2O of 1:1.[17m,18j,18k] The optimized solvent system for these conditions was found to be EtOH/H_2O after examining the biphasic systems, such as CH_3CN/H_2O,[18e,18f] DMF/H_2O,[16h,16,16m,16o,17j,17o,18g–18i] ROH/H_2O[16a,17k,17m,18i–18m] (ROH = MeOH, EtOH, *i*PrOH, and *t*BuOH; Entries 9–14). Reexamination of the biphasic system with EtOH/H_2O using an optimized volume ratio of 1:3 led to a better conversion of 97% within 10 min (Entry 15). The optimized base was found to be K_3PO_4 after trials with several bases such as K_3PO_4, KF, and Cs_2CO_3 (Entries 15–17). After examining the catalytic activities of **1**–**8** using the optimized conditions, **2** was found to exhibit the best conversion within 10 min (Entries 15, 18–25 in Table 1 and Figure S1). This might result from the bulkier substituents on the anilido group. The results also showed that acetate-containing **1**, **2**, and **4** were more active than chloride-containing **6**. Poor conversions were found with [*N*,*N*,*S*]-type **5** and **8**, indicating that a better interaction between the palladium center and the pendent sulfur atom might result in poor activities. However, the [*N*,*N*,*O*]-type **7** was more active than [*N*,*N*,*S*]-type **5** and **8**. Due to their poor solubility in the cosolvent system, poor activities were observed using type **VII 3** and **7′** as catalyst precursors. Complex **2** also demonstrated good conversions within 10–30 min for electronically deactivated substrates, even *ortho*-substituted aryl bromides (Entries 26–29). However, poor conversion was observed within 24 h using 2-bromomesitylene as the substrate under the optimized conditions at 50 °C (Entry 30), which might result from the steric effect of the substrate. A lower catalyst concentration (catalyst/substrate ratio of 10^{-4}:1) led to a conversion of 91% within 2 h at 50 °C (Entry 31), whereas a catalyst/substrate ratio of 10^{-5}:1 gave a poor conversion (30%) within 24 h at 80 °C (Entry 32). The turnover numbers (TONs) achieved were up to 9.1×10^3 and 3.0×10^4 using deactivated 4-bromoanisole as the substrate. Poor conversion (11%) was observed within 24 h at 80 °C using 4-chloroacetophenone as the substrate on a 1 mol-% scale with **2** (Entry 33). Comparing with some reports concerned with catalytic systems containing oxazoline groups or alcohol/H_2O for the Suzuki reaction, under optimized conditions **2** exhibited better activity than palladium complexes containing anilido-oxazoline[5d] and oxazoline ligands[17d–17f] and some catalytic systems using EtOH/H_2O as cosolvent, such as $Pd(OAc)_2$/guanidine[16a] and a (quinoline-8-carboxylato)palladium complex.[17m]



Scheme 4. Application of **1**–**8** to the Suzuki reaction.

Heck Reaction

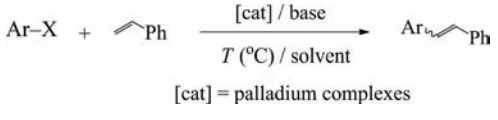
We also examined the catalytic activities of **1**–**8** in the Heck reaction using the coupling of aryl halides with styrene on a 1 mol-% Pd scale, as shown in Scheme 5. Selected results are listed in Table 2. When 4-bromoacetophenone was used as the substrate, the optimized base/solvent mixture for the reaction using **2** was found to be K_3PO_4/DMA after trials with a combination of bases (K_3PO_4, KF, and Cs_2CO_3) and solvents (THF, toluene, and DMA; Entries 1–

Table 1. Suzuki–Miyaura reaction catalyzed by **1**–**8**.[a]

Entry	Catalyst	Aryl halide	Base	Solvent	Pd [mol-%]	*T* [°C]	*t* [min]	Conv. [%][b]	Yield [%][c]
1	**2**	4-bromoanisole	K_3PO_4	toluene	1	room temp.	30	15	–
2	**2**	4-bromoanisole	K_3PO_4	THF	1	room temp.	30	7	–
3	**2**	4-bromoanisole	K_3PO_4	CH_2Cl_2	1	room temp.	30	13	–
4	**2**	4-bromoanisole	K_3PO_4	CH_3CN	1	room temp.	30	9	–
5	**2**	4-bromoanisole	K_3PO_4	DMF	1	room temp.	30	<5	–
6	**2**	4-bromoanisole	K_3PO_4	DMA	1	room temp.	30	<5	–
7	**2**	4-bromoanisole	K_3PO_4	MeOH	1	room temp.	30	28	–
8[d]	**2**	4-bromoanisole	K_3PO_4	H_2O	1	room temp.	30	12	–
9[d,e]	**2**	4-bromoanisole	K_3PO_4	CH_3CN/H_2O	1	room temp.	30	18	–
10[d,e]	**2**	4-bromoanisole	K_3PO_4	DMF/H_2O	1	room temp.	30	27	–
11[d,e]	**2**	4-bromoanisole	K_3PO_4	$MeOH/H_2O$	1	room temp.	30	87	83
12[d,e]	**2**	4-bromoanisole	K_3PO_4	$EtOH/H_2O$	1	room temp.	30	99	97
13[d,e]	**2**	4-bromoanisole	K_3PO_4	iPrOH/H_2O	1	room temp.	30	65	–
14[d,e]	**2**	4-bromoanisole	K_3PO_4	tBuOH/H_2O	1	room temp.	30	67	–
15[d,f]	**2**	4-bromoanisole	K_3PO_4	$EtOH/H_2O$	1	room temp.	10	97	92
16[d,f]	**2**	4-bromoanisole	KF	$EtOH/H_2O$	1	room temp.	10	22	–
17[d,f]	**2**	4-bromoanisole	Cs_2CO_3	$EtOH/H_2O$	1	room temp.	10	70	–
18[d,f]	**1**	4-bromoanisole	K_3PO_4	$EtOH/H_2O$	1	room temp.	10	90	83
19[d,f]	**3**	4-bromoanisole	K_3PO_4	$EtOH/H_2O$	1	room temp.	10	9	–
20[d,f]	**4**	4-bromoanisole	K_3PO_4	$EtOH/H_2O$	1	room temp.	10	84	80
21[d,f]	**5**	4-bromoanisole	K_3PO_4	$EtOH/H_2O$	1	room temp.	10	6	–
22[d,f]	**6**	4-bromoanisole	K_3PO_4	$EtOH/H_2O$	1	room temp.	10	78	–
23[d,f]	**7**	4-bromoanisole	K_3PO_4	$EtOH/H_2O$	1	room temp.	10	77	–
24[d,f]	**7′**	4-bromoanisole	K_3PO_4	$EtOH/H_2O$	1	room temp.	10	10	–
25[d,f]	**8**	4-bromoanisole	K_3PO_4	$EtOH/H_2O$	1	room temp.	10	5	–
26[d,f]	**2**	4-bromotoluene	K_3PO_4	$EtOH/H_2O$	1	room temp.	10	95	90
27[d,f]	**2**	4-tBu-bromobenzene	K_3PO_4	$EtOH/H_2O$	1	room temp.	30	90	85
28[d,f]	**2**	2-bromoanisole	K_3PO_4	$EtOH/H_2O$	1	room temp.	30	92	87
29[d,f]	**2**	2-bromotoluene	K_3PO_4	$EtOH/H_2O$	1	room temp.	30	93	90
30[d,f]	**2**	2-bromomesitylene	K_3PO_4	$EtOH/H_2O$	1	50	24 hr	13	–
31[d,f]	**2**	4-bromoanisole	K_3PO_4	$EtOH/H_2O$	0.01	50	2 hr	91	88
32[d,f]	**2**	4-bromoanisole	K_3PO_4	$EtOH/H_2O$	0.001	80	24 hr	30	–
33[d,f]	**2**	4-chloroacetophenone	K_3PO_4	$EtOH/H_2O$	1	80	24 hr	11	–

[a] Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), base (2.0 mmol), solvent (2 mL). [b] Determined by ^{1}H NMR spectroscopy. [c] Isolated yield (average of two runs). [d] Addition of 50 mol-% TBAB. [e] Volume ratio: 1:1. [f] Volume ratio: 1:3.

3). Poor conversion was observed when 4-bromoanisole was used as the substrate under the optimized base/solvent conditions (Entry 4). However, the conversion was enhanced up to 73% for 4-bromoanisole using similar conditions with the addition of 20 mol-% TBAB (Entry 5). The optimized conditions were used to examine the catalytic activities of **1**–**8**. The highest reactivity was observed for **6** with a conversion of up to 76% (Entries 5–13 in Table 2 and Figure S2). Compared with the trend of the Suzuki reaction, chloride-containing **6** and **7** were more active than acetate-containing **2** and **4**. Poor activities were also observed using type **VII 3** and **7′** due to their poor solubilities. Even under high temperature conditions, [*N*,*N*,*S*]-type **5** and **8** exhibited poor conversions probably due to the strong coordination between the palladium center and the pendent sulfur atom. Better conversions were achieved of up to 90% within 2.5 to 7 h for 4-bromoanisole, 4-bromotoluene, and 4-*tert*-butylbromobenzene using **6** under the optimized conditions (Entries 14–16). Lower catalyst concentrations of **6** were investigated on catalyst/substrate ratios from 10^{-3} to 10^{-4}:1 using 4-bromoacetophenone and 4-bromoanisole as the substrates. For the activated 4-bromoacetophenone, 93% conversion was achieved within 6 h with a 10^{-3}:1 ratio, however, it took 48 h to achieve 68% conversion with a 10^{-4}:1 ratio (Entries 17 and 19). The TONs achieved were up to 9.3×10^2 and 6.8×10^3. For the deactivated 4-bromoanisole, moderate conversion (60%) was achieved within 48 h with a 10^{-3}:1 ratio, whereas a poor conversion (< 5%) was obtained within 48 h with a 10^{-4}:1 ratio (Entries 18 and 20). The TON achieved was up to 6.0×10^2 using deactivated 4-bromoacetophenone as the substrate (Entry 18). Complex **6** also exhibited activity for catalyzing chlorinated substrates under the optimized conditions. A conversion of up to 94% within 4 h was achieved using activated 4-chloroacetophenone as a substrate (Entry 21); however, a poor conversion (5%) was observed using 4-chloroanisole as the substrate (Entry 22). Under the optimized conditions, **6** exhibited better catalytic activities than some palladium complexes containing anilido-oxazoline[5c,5d] and oxazoline ligands.[17d–17f]



Scheme 5. Application of **1**–**8** to the Heck reaction.

Table 2. Heck reaction catalyzed by **1**–**8**.[a]

Entry	Catalyst	Aryl halide	Base	Solvent	Pd [mol-%]	*T* [°C]	*t* [h]	Conv. [%][b]	Yield [%][c]
1	**2**	4-bromoacetophenone	KF	THF	1	70	1	5	–
2	**2**	4-bromoacetophenone	Cs_2CO_3	toluene	1	110	1	58	–
3	**2**	4-bromoacetophenone	K_3PO_4	DMA	1	135	1	97	91
4	**2**	4-bromoanisole	K_3PO_4	DMA	1	135	1	10	–
5[d]	**2**	4-bromoanisole	K_3PO_4	DMA	1	135	1	73	–
6[d]	**1**	4-bromoanisole	K_3PO_4	DMA	1	135	1	54	–
7[d]	**3**	4-bromoanisole	K_3PO_4	DMA	1	135	1	45	–
8[d]	**4**	4-bromoanisole	K_3PO_4	DMA	1	135	1	50	–
9[d]	**5**	4-bromoanisole	K_3PO_4	DMA	1	135	1	5	–
10[d]	**6**	4-bromoanisole	K_3PO_4	DMA	1	135	1	76	–
11[d]	**7**	4-bromoanisole	K_3PO_4	DMA	1	135	1	62	–
12[d]	**7′**	4-bromoanisole	K_3PO_4	DMA	1	135	1	34	–
13[d]	**8**	4-bromoanisole	K_3PO_4	DMA	1	135	1	10	–
14[d]	**6**	4-bromoanisole	K_3PO_4	DMA	1	135	2.5	90	85
15[d]	**6**	4-bromotoluene	K_3PO_4	DMA	1	135	3.5	90	84
16[d]	**6**	4-*tert*-butylbromobenzene	K_3PO_4	DMA	1	135	7	93	87
17[d]	**6**	4-bromoacetophenone	K_3PO_4	DMA	0.1	135	6	93	86
18[d]	**6**	4-bromoanisole	K_3PO_4	DMA	0.1	135	24	60	–
19[d]	**6**	4-bromoacetophenone	K_3PO_4	DMA	0.01	135	48	68	–
20[d]	**6**	4-bromoanisole	K_3PO_4	DMA	0.01	135	48	<5	–
21[d]	**6**	4-chlorooacetophenone	K_3PO_4	DMA	1	135	4	94	85
22[d]	**6**	4-chloroanisole	K_3PO_4	DMA	1	135	24	5	–

[a] Reaction conditions: aryl halide (1.0 mmol), styrene (1.3 mmol), base (1.5 mmol), solvent (2 mL). [b] Determined by ^{1}H NMR spectroscopy. [c] Isolated yield (average of two runs). [d] Addition of 20 mol-% TBAB.

Conclusions

A series of palladium anilido-oxazolinate complexes with or without pendant functionalities was synthesized and characterized. Based on the molecular structures, versatile bonding modes were found with different substituents on the anilido group. Due to the steric hindrance of the substituents on the anilido groups, **1** and **2** were observed as mononuclear complexes with a η^2-acetate group. The type **VII** bonding mode of dinuclear **3** with a η^1-acetate group is rare. Complex **4** was found to be a dinuclear complex with two bridging acetate ligands bearing the less bulky anilido group. For **5**, the palladium center was found to be surrounded by a tridentate ligand with a η^1-acetate group to complete the square-planar geometry. The palladium anilido-oxazolinate chloride complex **6**, which contains bulkier anilido groups, exhibited a dinuclear structure with two bridging chloride ions. However, the preparation of a palladium chloride complex from **4** resulted in a mixture of mononuclear **7** with coordination of the pendant methoxy functionality as the major product and dinuclear anilido-bridged palladium chloride complex **7′** as the minor product, in which the ligands coordinate to the metal centers in a similar bonding mode to **3**. Based on variable-temperature ^{1}H NMR spectroscopy, we proposed that **8** consists of two conformers in solution at room temperature. The catalytic activities of **1**–**8** towards the Suzuki and Heck reactions were examined. Under optimized conditions, **2** exhibited higher activity in the Suzuki reaction within 10 min at room temperature with 4-bromoanisole in a biphasic system of EtOH/H_2O. Complex **6** demonstrated better reactivity for 4-bromoanisole under optimized conditions in the Heck reaction. Based on these results, palladium anilido-oxazolinate complexes bearing bulkier substituents on the anilido group were found to be efficient catalyts in both Suzuki and Heck reactions.

Experimental Section

General Procedures and Instruments: All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk or drybox techniques. Toluene, THF, dichloromethane, and *n*-hexane were heated to reflux with the appropriate drying agent and distilled prior to use. Methanol, ethanol, 2-propanol, *tert*-butyl alcohol, acetonitrile, chloroform, DMF, and DMA were used as received. Deuterated solvents were dried with molecular sieves. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded with Varian Mercury-400 (400 MHz) or Varian Inova-600 (600 MHz) spectrometers in $CDCl_3$ or C_6D_6 at ambient temperature and referenced internally to the residual solvent peak and reported as parts per million relative to tetramethylsilane. Elemental analyses were performed with an Elementar Vario EL III instrument. HRMS (EI) were recorded with a Finnigan/Thermo Quest MAT 95XL spectrometer. $Pd(OAc)_2$ (Acros), K_3PO_4 (Lancaster), KF (Lancaster), Cs_2CO_3 (Lancaster), and TBAB (TCI) were used as supplied. Ligand precursors, $HNPh^{TriMe}Oxa$, $HNPh^{Di\text{-}iPr}Oxa$, $HNPh^{OMe}Oxa$, and $HNPh^{SMe}Oxa$, were prepared as described previously.[5g,5h]

($NPh^{TriMe}Oxa$)Pd(η^2-OAc) (1): To a flask containing $Pd(OAc)_2$ (0.32 g, 1.43 mmol) and $HNPh^{TriMe}Oxa$ (0.40 g, 1.3 mmol) was added THF (30 mL) at room temperature. The reaction mixture was heated to reflux for 14 h. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was evaporated to dryness. The crude product was washed with *n*-hexane (10 mL) to afford a green solid; yield 0.55 g (90%). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 1.46 [s, 6 H, oxazoline-C(CH_3)$_2$], 1.74 [s, 3 H, O–C(=O) –CH_3], 2.24 [s, 3 H, *p*-(CH_3)Ph], 2.28 [s, 6 H, *o*-(CH_3)$_2$Ph], 4.29 (s, 2 H, oxazoline-CH_2), 5.97 (d, *J* = 9.0 Hz, 1 H, Ph-*H*), 6.29

(t, J = 7.2 Hz, 1 H, Ph-*H*), 6.83 (m, 1 H, Ph-*H*), 6.90 (s, 2 H, Ph-*H*), 7.57 (m, 1 H, Ph-*H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 18.6 [s, *o*-(CH_3)$_2$Ph], 21.3 [s, *p*-(CH_3)Ph], 23.8 [s, O–C(=O)–CH_3], 28.1 [s, oxazoline-C(CH_3)$_2$], 67.7 [s, oxazoline-*C*(CH_3)$_2$], 80.0 (s, oxazoline-*C*H_2), 112.3, 115.3, 129.1, 129.5, 132.8 (s, *C*H-Ph), 103.6, 134.9, 136.5, 141.8, 151.0, 159.9 (C_{quat}), 191.5 [s, O-*C*(=O)-CH_3] ppm. $C_{22}H_{26}N_2O_3Pd$ (472.86): calcd. C 55.88, H 5.54, N 5.92; found C 56.42: H 5.80: N 6.29.

(NPh$^{Di/Pr}$Oxa)Pd(η^2-OAc) (2): To a flask containing $Pd(OAc)_2$ (0.25 g, 1.1 mmol) and HNPh$^{Di/Pr}$Oxa (0.35 g, 1.0 mmol) was added THF (30 mL) at room temperature. The reaction mixture was heated to reflux for 4 h. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was evaporated to dryness. The crude product was washed with *n*-hexane (10 mL) to afford a green solid; yield 0.44 g (85%). ^1H NMR ($CDCl_3$, 600 MHz): δ = 1.04 [d, J = 7.2 Hz, 6 H, (CH_3)$_2$CH], 1.46 [d, J = 6.6 Hz, 6 H, (CH_3)$_2$CH], 1.47 [s, 6 H, oxazoline-C(CH_3)$_2$], 1.70 [s, 3 H, O–C(=O)–CH_3], 3.54 [sept, 2 H, (CH$_3$)$_2$C*H*], 4.30 (s, 2 H, oxazoline-CH_2), 5.98 (d, J = 8.4 Hz, 1 H, Ph-*H*), 6.29 (m, 1 H, Ph-*H*), 6.81 (m, 1 H, Ph-*H*), 7.15 (d, J = 7.8 Hz, 2 H, Ph-*H*), 7.30 (t, J = 7.8 Hz, 1 H, Ph-*H*), 7.58 (dd, J = 8.4 & 1.2 Hz, 1 H, Ph-*H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 23.5 [s, O–C(=O)–*C*H$_3$], 24.03, 24.14 [s, (*C*H$_3$)$_2$CH], 28.1 [signal overlap, (CH$_3$)$_2$*C*H and oxazoline-C(*C*H$_3$)$_2$], 67.8 [s, oxazoline-*C*(CH$_3$)$_2$], 80.1 (s, oxazoline-*C*H_2), 112.3, 116.8, 123.7, 126.5, 129.4, 132.3 (s, *C*H-Ph), 103.1, 141.5, 147.1, 151.9, 160.0 (C_{quat}), 191.0 [s, O–*C*(=O)–CH$_3$] ppm. $C_{25}H_{32}N_2O_3Pd$ (514.94): calcd. C 58.31, H 6.26, N 5.44; found C 58.93, H 6.62, N 5.57.

[(μ-NPh^{H}Oxa)Pd(OAc)]$_2$ (3): To a flask containing $Pd(OAc)_2$ (0.25 g, 1.1 mmol) and HNPh^{H}Oxa (0.27 g, 1.0 mmol) was added toluene (10 mL) at room temperature. The mixture was stirred at 50 °C for 6 h. After cooling to room temperature, the reaction mixture was filtered, and the residue was evaporated to dryness. The crude product was washed with *n*-hexane (10 mL) to afford an orange solid; yield 0.33 g (77%). $C_{38}H_{40}N_4O_6Pd_2$ (861.56): calcd. C 52.97, H 4.68, N 6.50; found C 52.78, H 4.59, N 6.24. HRMS: calcd. for $C_{38}H_{40}N_4O_6Pd_2$ $[M + H]^+$ 861.1018; found 861.1082.

[(NPh^{OMe}Oxa)Pd(μ-OAc)]$_2$ (4): To a flask containing $Pd(OAc)_2$ (0.25 g, 1.1 mmol) and HNPh^{OMe}Oxa (0.30 g, 1.0 mmol) was added $CHCl_3$ (10 mL) at room temperature. The reaction mixture was stirred at 60 °C for 3 h. After cooling to room temperature, the reaction mixture was filtered, and the filtrate was evaporated off to dryness. The crude product was washed with *n*-hexane (10 mL) to afford a brown solid; yield 0.41 g (88%). ^1H NMR (C_6D_6, 600 MHz): δ = 1.11 [s, 6 H, oxazoline-C(CH_3)$_2$], 1.16 [s, 6 H, oxazoline-C(CH_3)$_2$], 1.26 [s, 6 H, O–C(=O)–CH_3], 3.36 (s, 6 H, OCH_3), 3.43 (s, 4 H, oxazoline-CH_2), 6.39 (m, 2 H, Ph-*H*), 6.59 (d, J = 9.0 Hz, 2 H, Ph-*H*), 6.63 (d, J = 7.2 Hz, 2 H, Ph-*H*), 6.82 (m, 2 H, Ph-*H*), 6.93 (m, 2 H, Ph-*H*), 7.11 (m, 2 H, Ph-*H*), 7.48 (d, J = 7.2 Hz, 2 H, Ph-*H*), 7.86 (d, J = 8.4 Hz, 2 H, Ph-*H*) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, 150 MHz): δ = 23.1 [s, O–C(=O)–*C*H$_3$], 27.4, [s, oxazoline-C(*C*H$_3$)$_2$], 27.8 [s, oxazoline-C(*C*H$_3$)$_2$], 55.2 (s, O*C*H$_3$), 67.7 [s, oxazoline-*C*(CH$_3$)$_2$], 79.6 (s, oxazoline-*C*H_2), 111.9, 113.0, 117.4, 121.6, 127.0, 129.8, 131.9, 132.9 (s, *C*H-Ph), 104.7, 136.7, 153.0, 157.0, 160.5 (C_{quat}), 191.4 [s, O–*C*(=O)–CH$_3$] ppm. $C_{40}H_{44}N_4O_8Pd_2$ (921.61): calcd. C 52.13, H 4.81, N 6.08; found C 52.15, H 4.82, N 5.94.

(NPh^{SMe}Oxa)Pd(OAc) (5): To a flask containing $Pd(OAc)_2$ (0.25 g, 1.1 mmol) and HNPh^{SMe}Oxa (0.32 g, 1.0 mmol) was added CH_2Cl_2 (30 mL) at room temperature. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was filtered, and the filtrate was evaporated to dryness. The crude product was washed with *n*-hexane (10 mL) to afford a purple solid; yield 0.47 g (99%). ^1H NMR ($CDCl_3$, 600 MHz): δ = 1.49 [s, 3 H, oxazoline-C(CH_3)$_2$], 1.68 [s, 3 H, oxazoline-C(CH_3)$_2$], 1.99 [s, 3 H, O–C(=O)–CH_3], 2.87 (s, 3 H, SCH_3), 4.15 (d, J = 8.4 Hz, 1 H, oxazoline-CH_2), 4.39 (d, J = 7.8 Hz, 1 H, oxazoline-CH_2), 6.61 (t, J = 7.2 Hz, 1 H, Ph-*H*), 6.65 (t, J = 7.8 Hz, 1 H, Ph-*H*), 7.03 (t, J = 8.4 Hz, 1 H, Ph-*H*), 7.09 (t, J = 8.4 Hz, 1 H, Ph-*H*), 7.25 (d, J = 8.4 Hz, 1 H, Ph-*H*), 7.33 (d, J = 7.2 Hz, 1 H, Ph-*H*), 7.44 (d, J = 7.8 Hz, 1 H, Ph-*H*), 7.60 (d, J = 8.4 Hz, 1 H, Ph-*H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 23.2 [s, O-C(=O)-*C*H$_3$], 26.5 [s, oxazoline-C(*C*H$_3$)$_2$], 27.9 [s, oxazoline-C(*C*H$_3$)$_2$], 30.7 (s, S*C*H$_3$), 68.8 [s, oxazoline-*C*(CH$_3$)$_2$], 81.4 (s, oxazoline-*C*H_2), 117.1, 119.1, 119.4, 120.6, 130.1, 130.2, 131.7, 132.5 (s, *C*H-Ph), 115.2, 124.7, 151.6, 158.9, 162.4 (C_{quat}), 177.6 [s, O–*C*(=O)–CH$_3$] ppm. $C_{20}H_{22}N_2O_3PdS$ (476.87): calcd. C 50.37, H 4.65, N 5.87; found C 49.72, H 4.74, N 5.84.

[(NPh$^{Di/Pr}$Oxa)Pd(μ-Cl)]$_2$ (6): To a flask containing **2** (0.26 g, 0.5 mmol) were added acetone (15 mL) and brine (15 mL) at room temperature. After stirring for 14 h, the green suspension was filtered, and the precipitate was washed with deionized water (10 mL) followed by *n*-hexane (10 mL) to afford a green solid; yield 0.24 g (98%). ^1H NMR ($CDCl_3$, 600 MHz): δ = 0.95 [d, J = 7.2 Hz, 12 H, (CH_3)$_2$CH], 1.13 [s, 12 H, oxazoline-C(CH_3)$_2$], 1.51 [d, J = 7.2 Hz, 12 H, (CH_3)$_2$CH], 3.42 [sept, 4 H, (CH$_3$)$_2$C*H*], 4.06 (s, 4 H, oxazoline-CH_2), 5.92 (d, J = 9.0 Hz, 2 H, Ph-*H*), 6.25 (m, 2 H, Ph-*H*), 6.75 (m, 2 H, Ph-*H*), 7.04 (d, J = 7.8 Hz, 2 H, Ph-*H*), 7.13 (t, J = 7.8 Hz, 2 H, Ph-*H*), 7.59 (dd, J = 8.4 and 1.2 Hz, 2 H, Ph-*H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 24.1, 24.5 [s, (*C*H$_3$)$_2$CH], 27.4 [s, oxazoline-C(*C*H$_3$)$_2$], 27.9 [s, (CH$_3$)$_2$*C*H], 70.1 [s, oxazoline-*C*(CH$_3$)$_2$], 80.8 (s, oxazoline-*C*H_2), 112.4, 117.3, 123.7, 125.7, 130.0, 132.1 (s, *C*H-Ph), 102.8, 146.0, 146.3, 151.7, 161.0 (C_{quat}) ppm. $C_{46}H_{58}Cl_2N_4O_2Pd_2$ (982.70): calcd. C 56.22, H 5.95, N 5.70; found C 55.87, H 6.19, N 5.91.

(NPh^{OMe}Oxa)Pd(Cl) (7): To a flask containing **4** (0.46 g, 0.5 mmol) were added acetone (15 mL) and brine (15 mL) at room temperature. After stirring for 1.5 h, the green suspension was filtered, and the residue was washed with deionized water (10 mL) followed by *n*-hexane (10 mL) to afford a green solid; yield 0.40 g (91%). ^1H NMR ($CDCl_3$, 600 MHz): δ = 1.69 [s, 6 H, oxazoline-C(CH_3)$_2$], 4.15 (s, 3 H, OCH_3), 4.30 (br., 2 H, oxazoline-CH_2), 6.61 (t, J = 7.2 Hz, 1 H, Ph-*H*), 6.74 (m, 1 H, Ph-*H*), 6.86 (m, 1 H, Ph-*H*), 7.02 (d, J = 8.4 Hz, 1 H, Ph-*H*), 7.13 (m, 1 H, Ph-*H*), 7.42 (m, 1 H, Ph-*H*), 7.54 (d, J = 8.4 Hz, 1 H, Ph-*H*), 7.59 (dd, J = 7.8 & 1.2 Hz, 1 H, Ph-*H*) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 150 MHz): δ = 27.4 [s, oxazoline-C(*C*H$_3$)$_2$], 61.8 (s, O*C*H$_3$), 69.7 [s, oxazoline-*C*(CH$_3$)$_2$], 81.4 (s, oxazoline-*C*H_2), 113.7, 116.0, 116.3, 120.0, 120.3, 123.4, 130.1, 132.9 (s, *C*H-Ph), 112.9, 140.2, 149.6, 154.7, 161.5 (C_{quat}) ppm. $C_{18}H_{19}ClN_2O_2Pd$ (437.21): calcd. C 49.45, H 4.38, N 6.41; found C 49.88, H 4.82, N 6.74.

[(μ-NPh^{OMe}Oxa)Pd(Cl)]$_2$ (7′): To a flask containing **7** (0.26 g, 0.60 mmol) was added toluene (3.0 mL) at room temperature. The reaction mixture was stirred at 80 °C for 2.5 d. After cooling to room temperature, the brown suspension was filtered, and the residue was washed with toluene (10 mL) to afford an orange solid; yield 0.20 g (77%). ^1H NMR ($CDCl_3$, 600 MHz): δ = 0.90 [s, 6 H, oxazoline-C(CH_3)$_2$], 1.36 [s, 6 H, oxazoline-C(CH_3)$_2$], 3.61 [s, 6 H, *o*-(OCH_3)Ph], 3.65 (d, J = 8.4 Hz, 2 H, oxazoline-CH_2), 4.00 (d, J = 8.4 Hz, 2 H, oxazoline-CH_2), 5.66 (d, J = 8.0 Hz, 2 H, Ph-*H*), 6.33 (t, J = 7.2 Hz, 2 H, Ph-*H*), 6.88 (t, J = 7.6 Hz, 2 H, Ph-*H*), 6.95 (d, J = 8.0 Hz, 2 H, Ph-*H*), 7.48 (t, J = 7.6 Hz, 2 H, Ph-*H*), 7.61 (d, J = 6.8 Hz, 2 H, Ph-*H*), 7.91 (t, J = 8.0 Hz, 2 H, Ph-*H*), 9.67 (d, J = 8.4 Hz, 2 H, Ph-*H*) ppm. $C_{36}H_{38}Cl_2N_4O_4Pd_2$ (874.43): calcd. C 49.45, H 4.38, N 6.41; found C 49.07, H 4.75, N 6.43.

(NPh^{SMe}Oxa)Pd(Cl) (8): To a flask containing **5** (0.17 g, 0.36 mmol) were added acetone (10 mL) and brine (10 mL) at room temperature. After stirring for 0.5 h, the purple suspension was filtered, and the precipitate was washed with deionized water (10 mL) and *n*-hexane (10 mL) to afford a purple solid; yield 0.12 g (71%). A ratio of 1.33:1 was displayed for the two isomers in C_6D_6. For the major isomer: ^{1}H NMR (C_6D_6, 600 MHz): δ = 1.58 [s, 3 H, oxazoline-C(CH_3)$_2$], 1.61 [s, 3 H, oxazoline-C(CH_3)$_2$], 2.00 [s, 3 H, *o*-(SCH_3)Ph], 3.29 (d, *J* = 7.8 Hz, 1 H, oxazoline-CH_2), 3.58 (d, *J* = 8.4 Hz, 1 H, oxazoline-CH_2), 6.32 (t, *J* = 7.2 Hz, 1 H, Ph-*H*), 6.54 (signal overlap, 1 H, Ph-*H*), 6.70 (t, *J* = 7.5 Hz, 1 H, Ph-*H*), 6.76 (d, *J* = 7.2 Hz, 1 H, Ph-*H*), 6.89 (m, 1 H, Ph-*H*), 7.25 (d, *J* = 8.4 Hz, 1 H, Ph-*H*), 7.40 (d, *J* = 9.0 Hz, 3 H, Ph-*H*), 7.70 (t, *J* = 6.3 Hz, 1 H, Ph-*H*) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ = 27.8 [s, *o*-(S*C*H$_3$)Ph], 27.37 [s, oxazoline-C(*C*H$_3$)$_2$], 28.2 [s, oxazoline-C(*C*H$_3$)$_2$], 70.1 (C_{quat}), 81.4 (s, oxazoline-CH_2), 117.4, 118.6, 120.2, 121.5, 128.8, 130.5, 132.8 (s, *C*H-Ph), 115.9, 123.5, 152.3, 159.8, 162.7 (C_{quat}) ppm. For the minor isomer: ^{1}H NMR (C_6D_6, 600 MHz): δ = 1.60 [s, 3 H, oxazoline-C(CH_3)$_2$], 1.63 [s, 3 H, oxazoline-C(CH_3)$_2$], 2.36 [s, 3 H, *o*-(SCH_3)Ph], 3.31 (d, *J* = 7.8 Hz, 1 H, oxazoline-CH_2), 3.60 (d, *J* = 8.4 Hz, 1 H, oxazoline-CH_2), 6.38 (t, *J* = 7.2 Hz, 1 H, Ph-*H*), 6.54 (signal overlap, 2 H, Ph-*H*), 6.66 (t, *J* = 7.5 Hz, 1 H, Ph-*H*), 6.83 (m, 1 H, Ph-*H*), 7.21 (d, *J* = 8.4 Hz, 1 H, Ph-*H*), 7.37 (d, *J* = 9.0 Hz, 1 H, Ph-*H*), 7.70 (t, *J* = 6.3 Hz, 1 H, Ph-*H*) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ = 24.7 [s, *o*-(S*C*H$_3$)Ph], 27.41 [s, oxazoline-C(*C*H$_3$)$_2$], 28.4 [s, oxazoline-C-(*C*H$_3$)$_2$], 70.2 (C_{quat}), 81.5 (s, oxazoline-CH_2), 117.5, 119.1, 120.5, 121.4, 129.6, 130.7, 132.5 (s, *C*H-Ph), 116.5, 125.9, 152.5, 158.1, 162.5 (C_{quat}) ppm. $C_{18}H_{19}ClN_2OPdS$ (453.27): calcd. C 47.69, H 4.22, N 6.18; found C 47.99, H 4.33, N 6.02.

General Procedure for the Suzuki Reaction: The prescribed amount of catalyst, base (2 equiv.), phenylboronic acid (1.5 equiv.), and solid aryl halides (1 equiv.) were placed in a Schlenk tube under nitrogen. Ethanol (0.5 mL), deionized water (1.5 mL), and liquid aryl halides (1 equiv.) were added by syringe. The reaction mixture was stirred at the prescribed temperature for the prescribed time. The volatiles were removed, and the residue was diluted with ethyl acetate and filtered through a pad of silica gel. A sample in $CDCl_3$ was taken for determination of conversion by NMR spectroscopy. The crude material was further purified by flash chromatography on silica gel (ethyl acetate/*n*-hexane).

General Procedure for the Heck Reaction: The prescribed amount of catalyst, base (1.5 equiv.), and solid aryl halides (1 equiv.) were placed in a Schlenk tube under nitrogen. Solvent (2 mL), styrene (1.3 equiv.), and liquid aryl halides (1 equiv.) were added by syringe. The reaction mixture was heated to the prescribed temperature for the prescribed time. The volatiles were removed, and the residue was dissolved in ethyl acetate and filtered through a pad of silica gel. A sample in $CDCl_3$ was taken for determination of conversion by NMR spectroscopy. The crude material was further purified by flash chromatography on silica gel (ethyl acetate/*n*-hexane).

Crystal Structure Data: Crystals were grown from concentrated CH_2Cl_2/*n*-hexane solutions (for **4**–**8** and **7′**) or *n*-hexane solutions (for **1** and **2**) and isolated by filtration. Suitable crystals of **1**–**5**, **7′**, and **8** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Suitable crystals of **6** and **7** were mounted on a Mounted CryoLoop (Hampton Research, size: 0.5–0.7 mm) using perfluoropolyether vacuum oil (Aldrich, Fomblin®Y) and cooled rapidly in a stream of cold nitrogen gas using an Oxford Diffraction Limited GEMINT R and S. For **1**–**5**, **7′**, and **8**, the absorption correction was based on the symmetry equivalent reflections using the SADABS program.[19] For **6** and **7**, empirical absorption correction was based on spherical harmonics implemented in SCALE3 ABSPACK scaling algorithm from CrysAlis RED, Oxford Diffraction Ltd. The space group determination was based on the Laue symmetry and systematic absences and was confirmed using the structure solution. The structures were solved by direct methods using a SHELXTL package.[20] All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Some details of the data collection and refinement are given in Tables S1 and S2.

CCDC-762654 (for **1**), -762655 (for **2**), -833347 (for **3**), -762656 (for **4**), -762657 (for **5**), -762658 (for **6**), -762659 (for **7**), -762660 (for **7′**), and -762661 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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