

# Synthesis and Characterization of Silver and Palladium Complexes with Xanthene-Based N-Heterocyclic Carbene–Oxazoline Ligands

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We synthesized xanthenes substituted with two different donor ligand units, N-heterocyclic carbene (NHC) and oxazoline, by the sequential coupling reaction. Silver complexes 15 and 19 were prepared by the reaction between the xanthene derivatives and  $Ag_2O$ . Pd complexes 16 and 20 were also synthesized by the reaction of the corresponding silver complexes with Pd(PhCN)<sub>2</sub>Cl<sub>2</sub>. X-ray crystallographic analysis revealed that complexes 15-PF<sub>6</sub>, 16, and 20 adopted *trans* configurations, while the Ag atom of 15-Cl coordinated only to the NHC ligand.

#### Introduction

A large number of multidentate ligands that have more than two different coordinating units have been reported, and their metal complexes have been widely used as homogeneous catalysts. Some metal complexes with bidentate N-heterocyclic carbene (NHC)-oxazoline ligands turned out to be very efficient catalysts (Chart 1).<sup>1</sup> Herrmann and coworkers reported the first example of an NHC/oxazoline bidentate ligand, which was tethered by a methylene group.<sup>2</sup> The syntheses of similar ligands have also been reported, and various metals, such as Pd, Pt, Rh, and Ir, were incorporated. The catalytic activities of those complexes, especially for asymmetric reactions, have been investigated.<sup>3-6</sup> The structures of some palladium complexes have been studied by X-ray crystallographic analysis. Herrmann's complex<sup>2</sup> was a dimeric species with trans geometry, although other complexes with restricted backbone structure adopted cis geometry (Chart 1).

We recently reported the synthesis of bidentate bis(NHC)palladium complex 7 with a xanthene framework. The complex

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Chart 1. Examples of N-Heterocyclic Carbene-Oxazoline Ligands and the Pd Complexes



had conformational chirality in the solid state due to its sterical hindrance, and the palladium complexes adopted a *trans* conformation.<sup>7</sup> Although there are many reports concerning bis(phosphine),<sup>8</sup> bis(NHC),<sup>7</sup> and bis(oxazoline) ligands<sup>9</sup> with the xanthene framework, bidentate ligands consisting of two different ligand units are rare,<sup>10</sup> and there is no precedent of the

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Figure 1

Scheme 1. Synthesis of Ligand 14 and Metal Complexes



xanthene derivative with an NHC and oxazoline unit. A bidentate NHC ligand incorporating an oxazoline unit based on the

Scheme 2. Synthesis of 18–20



xanthene framework would be interesting from a structural perspective: the palladium complex would adopt a *trans* conformation.<sup>11</sup> In this paper, we report the synthesis and structural analysis of Ag and Pd complexes with new NHC– oxazoline ligands (Figure 1).

#### Synthesis of the Complexes

The syntheses of Ag complex 15 and Pd complex 16 are summarized in Scheme 1. 4,5-Bis(trimethylsilyl)-9,9-dimethylxanthene  $(8)^{12}$  reacted with bromine (1.3 equiv) in the presence of pyridine to afford 9 in good yield. It is noteworthy that the monobromination of 8 proceeded predominantly and the dibrominated xanthene was not observed. The remaining trimethylsilyl group was converted to a B(OH)<sub>2</sub> group by the reaction of 9 with BBr<sub>3</sub> and H<sub>2</sub>O. Compound 11 was prepared by the Suzuki-Miyaura coupling reaction of 10 with 4-iodophenyloxazoline, which reacted with diamine derivative 12 in the presence of a Pd catalyst to afford 13 in 85% yield. Imidazolinium salt 14 was synthesized by the reaction of 13 with HC(OEt)<sub>3</sub> under acidic conditions. Silver complex 15-Cl was prepared by the reaction of an imidazolium salt with Ag<sub>2</sub>O, and the anion exchange was accomplished by the treatment of 15-Cl with an aqueous solution of KPF<sub>6</sub> to afford 15-PF<sub>6</sub>. Palladium complex 16 was synthesized by the Ag-Pd exchange reaction of Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> and silver complex 15-Cl.

Pd complex 20, with a less bulky NHC ligand, containing imidazolium instead of an imidazoline group to facilitate the synthesis, was also prepared (Scheme 2). The coupling reaction of 11 and 17 afforded the imidazole derivative 18 in moderate yield. Alkylation of 18 with MeI gave the imidazolium salt, and the PF<sub>6</sub> salt of the Ag complex (19) was prepared by treatment of the imidazolium salt with Ag<sub>2</sub>O

<sup>(11)</sup> To the best of our knowledge, no study has been reported for the structural analysis of the nontethered NHC-oxazoline Pd complex. Therefore, it is not clear whether these Pd complexes naturally prefer to form *trans* complexes. We assume that these complexes prefer to form *trans* complexes since several nontethered *trans* NHC-pyridine Pd complexes and a *trans* NHC-imidazole Pd complex and a dinuclear *trans* NHC-oxazole Pd complex (ref 2) have been reported in the literature. See: (a) O'Brien, C. J.; Kantchev, E. A. B.; Valente, C.; Hadei, N.; Chass, G. A.; Lough, A.; Hopkinson, A. C.; Organ, M. G. *Chem.*-*Eur. J.* **2006**, *12*, 4743-4748. (b) Batey, R. A.; Shen, M.; Lough, A. J. Org. *Lett.* **2002**, *4*, 1411-1414.

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Figure 2. <sup>13</sup>C NMR spectra of 14 (top), 15-Cl (middle), and 15-PF<sub>6</sub> (bottom) in CDCl<sub>3</sub> at room temperature.

and ion exchange. The palladium complex **20** was synthesized by the reaction of **19** with  $Pd(PhCN)_2Cl_2$  and  $Et_4NCl$ .

It is noteworthy that all Ag and Pd complexes, 15-Cl, 15- $PF_6$ , 16, and 20, were bench-stable compounds, and it was not necessary to use dehydrated solvent or carry out the reaction under inert atmosphere for the synthesis of these compounds.

#### **Characterization of the Complexes**

Complexes 15-Cl, 15-PF<sub>6</sub>, 16, and 20 were characterized by NMR spectra, mass spectra, and X-ray analyses. Inspection of <sup>13</sup>C NMR spectra revealed a significant change of the chemical shift between carbene precursor 14 and carbene complexes 15-Cl and 15-PF<sub>6</sub> (Figure 2). The NMR resonance of the carbene carbon nuclei of both carbene complexes, 15-Cl and 15-PF<sub>6</sub>, drastically shifted downfield from that of 14, and they were observed as two doublets with characteristic coupling constants ( $J_C^{107}{}_{Ag} \approx 225$  Hz and  $J_C^{109}{}_{Ag} \approx$ 260 Hz). This shift indicates the formation of the carbene complex. In contrast, the chemical shifts of oxazoline N=C-O of 15-Cl and 15-PF<sub>6</sub> were significantly different. The chemical shift of the N=C-O carbon nuclei of 15-Cl (164.4 ppm) was similar to that of 14 (165.5 ppm), although the corresponding peak of 15-PF<sub>6</sub> (171.4 ppm) shifted downfield.<sup>13</sup> This difference implied that the oxazoline moiety coordinated to Ag in 15-PF<sub>6</sub> but not in 15-Cl.

This speculation was confirmed by X-ray crystal structural analysis. The crystal structures of Ag complexes as 15-Cl and 15-PF<sub>6</sub> are shown in Figures 3 and 4. The X-ray analysis

revealed that the oxazoline ligand of **15-Cl** did not coordinate to the silver atom, but the chloride ion did. This trend that the halogen atom coordinates to the metal instead of the oxazoline ligand due to its strong nucleophilicity was also reported in several NHC–oxazoline ligands.<sup>6e</sup> On the other hand, both NHC and oxazoline moieties **15-PF**<sub>6</sub> were coordinated to the silver atom, and the complex adopted a *trans*-coordinated geometry (bite angle: 175°). The X-ray analysis of **15-PF**<sub>6</sub> also revealed that the dihedral angle between NHC (N–C–N plane) and oxazoline (C=N–C plane) was 28.1°, and the torsion angle between C–(Ag)–N and C<sub>4-xan</sub>–C<sub>5-xan</sub> was 24.8°. Thus the complex adopted a twisted structure.<sup>14</sup>

Structures of Pd complexes **16** and **20** are shown in Figures 5 and 6. The representative structural parameters of Pd complexes are summarized in Table 1. The geometry at the Pd center of these complexes is square-planar, and the oxazoline unit is coordinated to palladium at the *trans*-position of the NHC unit (bite angle: 178° for **16**, 175° for **20**). The dihedral angle ( $\theta_1$ ) between NHC and oxazoline was 8.3° for **16** and 10.7° for **20**, and the torsion angle ( $\theta_2$ ) between C–(Pd)–N and C<sub>4-xan</sub>–C<sub>5-xan</sub> was 7.1° for **16** and 2.4° for **20**. This result indicates that Pd complexes **16** and **20** adopted an almost planar structure, which was in stark contrast with the twisted one of **7** ( $\theta_1 = 31.1^\circ$ ,  $\theta_2 = 28.9^\circ$ ).<sup>7</sup> Thus the replacement of NHC with oxazoline, from **7** to **16**, resulted in the decrease of both the dihedral angle and the torsion angle. The replacement

<sup>(13)</sup> Poor solubility of **20** in  $\text{CDCl}_3$  made comparison of the NMR spectra of **20** with **15-PF**<sub>6</sub> impossible, but the chemical shift of N=*C*-O carbon nuclei in  $\text{CD}_2\text{Cl}_2$  was 171.7 ppm, and this is close to that of **15-PF**<sub>6</sub> rather than that of **15-C**I.

<sup>(14)</sup> A referee pointed out that infrared spectroscopy is a nice method to study the binding of an oxazoline onto a metal. We compared the infrared spectroscopy of several compounds ( $13 (1645 \text{ cm}^{-1}), 14 (1632 \text{ cm}^{-1}), 15$ -Cl (1646 cm<sup>-1</sup>), and 15-PF<sub>6</sub> (1634 cm<sup>-1</sup>)) and found that the values of the C=N stretching vibrations were different. However, it is difficult to determine whether the binding of an oxazoline onto a metal is present by infrared spectroscopy in this study. It is also possible that the exchange of the anion occurred during the observation of IR of the compounds in KBr pellet.



**Figure 3.** Thermal ellipsoid model of the crystal structure of **15-CI**. Front view (a) and bottom view (b). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag(1)-C(1) = 2.082(2), Ag(1)-Cl(1) = 2.3259(7), C(1)-Ag(1)-Cl(1) = 171.24(6).

of the 2,6-diisopropylphenyl group with the methyl group, from **16** to **20**, induced a further decrease of the torsion angle. The bond length between Pd and the NHC carbene carbon (1.951 Å for **16** and 1.970 Å for **20**) was significantly shorter than that of **7** (2.048 Å). This indicates the existence of a stronger Pd-carbene carbon bond of the NHC-oxazoline Pd complex than that of the NHC-NHC Pd complex. This could be attributed to the less steric hindrance and/or the *trans* effect of the oxazoline ligand of the NHC-oxazoline complex.

### Conclusion

We synthesized a new class of xanthene-bridged bidentate complexes that are composed of NHC and oxazoline ligands. The X-ray crystallographic analyses revealed the complex had a planar *trans* geometry. In view of the catalyst development for various reactions, especially for the asymmetric synthesis, the study toward the synthesis of various nonracemic metal complexes and the examination of catalytic activity of these complexes are desirable and currently under way.

## **Experimental Section**

**General Procedures.** 4,5-Bis(trimethylsilyl)-9,9-dimethylxanthene (8),<sup>13</sup> 4-iodophenyloxazoline,<sup>15</sup> and Pd(PhCN)<sub>2</sub>Cl<sub>2</sub><sup>16</sup> were prepared



**Figure 4.** Thermal ellipsoid model of the crystal structure of **15**-**PF**<sub>6</sub>. Front view (a) and bottom view (b). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms, PF<sub>6</sub> anions, and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ag(1)-C(1) = 2.062(3), Ag(1)-N(3) = 2.099(2), C(1)-Ag(1)-N(3) = 175.0(1).

according to the reported procedure. Other reagents were commercially available and used without further purification. Chemical shifts were reported in delta units ( $\delta$ ) relative to chloroform-*d* (7.24 ppm for <sup>1</sup>H NMR, 77.0 ppm for <sup>13</sup>C NMR) and DMSO*d*<sub>6</sub> (2.49 ppm for <sup>1</sup>H NMR, 39.7 ppm for <sup>13</sup>C NMR). Multiplicity is indicated by s (singlet), d (doublet), t (triplet), or m (multiplet).

**4-Bromo-5-trimethylsilyl-9,9-dimethylxanthene (9).** To a solution of 4,5-bis(trimethylsilyl)-9,9-dimethylxanthene (8) (10.6 g, 30 mmol) and pyridine (3.2 mL, 39 mmol) in anhydrous  $CH_2Cl_2$  (150 mL) was added dropwise bromine (2.0 mL, 39 mmol) in anhydrous  $CH_2Cl_2$  (50 mL) over 1 h at -78 °C under an argon atmosphere. After stirring for 2 h, the mixture was warmed to room temperature. Aqueous NaHSO<sub>3</sub> (5% solution, 100 mL) was added, and the aqueous layer was extracted with  $CH_2Cl_2$  (50 mL × 2). The combined organic layer was dried over MgSO<sub>4</sub> and filtered. The filtrate was concentrated, and the residue was washed with hexane to afford **9** (7.73 g, 71%) as a colorless powder: mp 142.5–144.0 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) 7.44 (dd, J = 7.8, 1.8 Hz, 1H), 7.42 (dd, J = 7.2, 1.8 Hz, 1H), 7.34 (dd,

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**Figure 5.** Thermal ellipsoid model of the crystal structure of **16**. Front view (a) and bottom view (b). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)-C(1) = 1.951(5), Pd(1)-N(3) = 2.088(4), Pd(1)-Cl(1) = 2.307(1), Pd(1)-Cl(2) = 2.302(1), C(1)-Pd(1)-N(3) = 178.0(2), C(1)-Pd(1)-Cl(1)=89.7(1), C(1)-Pd(1)-Cl(2)=90.3(1), N(3)-Pd(1)-Cl(1) = 91.7(1), N(3)-Pd(1)-Cl(2) = 88.2(1), Cl(1)-Pd(1)-Cl(2) = 178.32(5).

J = 7.2, 1.8 Hz, 1H), 7.33 (dd, J = 7.2, 1.8 Hz, 1H), 7.10 (t, J = 7.2 Hz, 1H), 6.92 (t, J = 7.8 Hz, 1H), 1.62 (s, 6H), 0.46 (s, 9H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 154.2, 147.5, 133.4, 131.8, 131.5, 128.4, 127.6, 127.3, 125.4, 123.5, 123.4, 110.2, 34.6, 32.9, -0.7; IR (KBr) 3053, 2947, 1561, 1445, 1405, 1280, 1246, 1192, 1142, 1102, 1062 cm<sup>-1</sup>; Anal. Calcd for C<sub>18</sub>H<sub>21</sub>BrOSi: C, 59.83; H, 5.86. Found: C, 59.53; H, 5.77.

4-Bromo-9,9-dimethylxanthene-5-boronic Acid (10). To a solution of 9 (6.76 g, 18.7 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added BBr<sub>3</sub> (2.1 mL, 22.4 mmol), and the mixture was stirred for 24 h. Water (30 mL) was slowly added, and the biphasic mixture was stirred for 1 h at room temperature. The organic layer was separated, and the aqueous layer was extracted with  $CH_2Cl_2$  (20 mL  $\times$  2). The combined organic layer was dried over MgSO<sub>4</sub>, and the filtrate was concentrated. The product was purified by column chromatography (silica gel, hexane/AcOEt (6:1)) to afford 10 (5.32 g, 85%) as a colorless powder: mp 118.7–119.0 °C; <sup>1</sup>H NMR (600 MHz, DMSO- $d_6$ ) 7.44 (dd, J =7.8, 1.8 Hz, 1H), 7.93 (s, 2H), 7.60 (dd, J = 7.8, 1.2 Hz, 1H), 7.58 (dd, J = 7.8, 1.2 Hz, 1H), 7.54 (dd, 7.8, 1.2 Hz, 1H), 7.48 (dd, J = 7.2, 1.2 Hz, 1H), 7.14 (t, J = 7.2 Hz, 1H), 7.07 (t, J = 7.8 Hz, 1H), 1.58 (s, 6H); <sup>13</sup>C NMR (150 MHz, DMSO-d<sub>6</sub>) 152.8, 146.4, 133.5, 132.1, 131.2, 129.0, 128.4, 126.3, 124.6, 123.8, 109.5, 34.5, 32.4; IR (KBr) 3555, 3413, 2978, 1566, 1423, 1330, 1282, 1249, 1043,



**Figure 6.** Thermal ellipsoid model of the crystal structure of **20**. Front view (a) and bottom view (b). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)-C(1) = 1.966(4), Pd(1)-N(3) = 2.063(3), Pd(1)-Cl(1) = 2.314(1), Pd(1)-Cl(2) = 2.310(1), C(1)-Pd(1)-N(3)=175.0(1), C(1)-Pd(1)-Cl(2) = 89.9(1), N(3)-Pd(1)-Cl(1) = 94.2(1), N(3)-Pd(1)-Cl(2) = 87.8(1), Cl(1)-Pd(1)-Cl(2) = 177.97(4).

Table 1. Selected Bond Length (Å) and Angles (deg) of 7, 16,and 20

complex	Pd-C <sup>a</sup>	$Pd-N^b$	$\theta_1{}^c$	$\theta_2^{d}$
$7^{e}$	2.048		31.1	28.9
16	1.951	2.087	8.3	7.1
20	1.970	2.063	10.7	2.4

<sup>*a*</sup> Bond length between C<sub>carbene</sub> and Pd. <sup>*b*</sup> Bond length between N<sub>oxazoline</sub> and Pd. <sup>*c*</sup> Dihedral angle between N–C–N plane and N'–C'–N' plane (NHC) or C'–N'–C' plane (oxazoline). <sup>*d*</sup> Torsion angle between C4<sub>xan</sub>– C5<sub>xan</sub> and C<sub>carbene</sub>–(Pd)–C'<sub>carbene</sub> (or C<sub>carbene</sub>–(Pd)–N<sub>oxazoline</sub>). <sup>*e*</sup> Data were collected from ref 7a. The structural data of a crystal obtained by recrystallization from cyclohexane were used.

1018 cm $^{-1}$ . Anal. Calcd for  $C_{15}H_{14}BBrO_3:$  C, 54.10; H, 4.24. Found: C, 54.05; H, 4.33.

**Oxazoline Derivative 11.** A mixture of **10** (1.76 g, 5.3 mmol), 4-iodophenyloxazoline (1.45 g, 5.3 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (312 mg, 0.27 mmol), and K<sub>2</sub>CO<sub>3</sub> (885 g, 6.4 mmol) in DME (9 mL) and water (3 mL) was heated to 100 °C for 6 h under an argon atmosphere. The crude product was extracted with diethyl ether (20 mL  $\times$  2), and the organic layer was dried over MgSO<sub>4</sub>. The filtrate was concentrated and purified by column chromatography (silica gel, hexane/AcOEt (4:1)) to afford **11** (1.89 g, 82%) as a colorless solid: mp 113.5–114.3 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) 8.02 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 7.8 Hz, 2H), 7.42 (dd, J = 7.8, 1.8 Hz, 1H), 7.39 (dd, J = 7.8, 1.8 Hz, 1H), 7.34 (dd, J = 7.8, 1.8 Hz, 1H), 7.29 (dd, J = 7.8, 1.8 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 6.93 (t, J = 7.8 Hz, 1H), 4.45 (t, J = 9.6 Hz, 2H), 4.09 (t, J = 9.0 Hz, 2H), 1.65 (s, 6H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) 164.7, 147.4, 147.2, 140.4, 132.0, 131.3, 130.6, 130.2, 129.2, 129.0, 127.7, 126.4, 125.6, 124.8, 123.9, 123.6, 110.8, 67.6, 55.0, 34.9, 32.1; IR (KBr) 2962, 1644, 1399, 1353, 1239 cm<sup>-1</sup>. Anal. Calcd for C<sub>24</sub>H<sub>20</sub>BrNO<sub>2</sub>: C, 66.37; H, 4.64; N, 3.22. Found: C, 66.57; H, 4.84; N, 3.17.

Boronate 12. To a suspension of N-(4-iodo-2,6-diisopropyl)-N'-(2,6-diisopropyl)oxamide<sup>7a</sup> (7.48 g, 14 mmol) and NaBH<sub>4</sub> (3.18 g, 84 mmol) in anhydrous THF (120 mL) was slowly added BF<sub>3</sub>·OEt<sub>2</sub> (13.8 mL, 112 mmol) at ambient temperature. The mixture was stirred for 1 h at ambient temperature, and then the mixture was heated to reflux for 18 h. The mixture was quenched with MeOH (12 mL) and concentrated HCl (3 mL) at 0 °C. All volatiles were removed by evaporation, and aqueous NaOH (1 M, 150 mL) was added to the residue. The mixture was extracted with diethyl ether (100 mL  $\times$  3), and the combined organic layer was dried over MgSO<sub>4</sub> and evaporated. The crude product was purified by column chromatography (silica gel, hexane/AcOEt (25:1)) to afford N-(4-iodo-2,6-diisopropylphenyl)-N'-(2,6-diisopropylphenyl)ethylenediamine (6.46 g, 67%) as a colorless solid: mp 63.8-65.0 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 7.36 (s, 2H), 7.12-7.03 (m, 3H), 3.36-3.21 (m, 6H), 3.11 (s, 4H), 1.24 (d, J = 6.9 Hz, 12H), 1.21 (d, J = 6.9 Hz, 12H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) 145.0, 143.3, 143.0, 142.5, 133.0, 124.0, 123.6, 88.4, 52.1, 27.7, 24.2, 24.0; IR (KBr) 3370, 2963, 2866, 1444, 1247, 1191 cm<sup>-1</sup> Anal. Calcd for C<sub>26</sub>H<sub>39</sub>IN<sub>2</sub>: C, 61.65; H, 7.76; N, 5.53. Found: C, 61.69; H, 7.72; N, 5.27.

To a suspension of N-(4-iodo-2,6-diisopropylphenyl)-N'-(2,6diisopropylphenyl)ethylenediamine (2.28 g, 4.5 mmol) and Pd-(dppf)Cl<sub>2</sub> (97.8 mg, 0.135 mmol) in anhydrous dioxane (20 mL) were added pinacolborane (1.9 mL, 6.75 mmol) and NEt<sub>3</sub> (1.9 mL, 13.5 mmol). After the mixture was heated at 80 °C for 12 h, water (20 mL) was added. The product was extracted with diethyl ether (20 mL  $\times$  2), and the organic layer was dried over MgSO<sub>4</sub>. The filtrate was concentrated, and the product was purified by column chromatography (silica gel, hexane/AcOEt (25:1)) to afford 12 (1.68 g, 74%) as a colorless solid: mp 125.8–126.0 °C; <sup>1</sup>H NMR (300 MHz) 7.56 (s, 2H), 7.12-7.03 (m, 3H), 3.37-3.26 (m, 4H), 3.18-3.14 (m, 4H), 1.32 (s, 12H), 1.27 (d, J = 6.9 Hz, 12H), 1.23 (d, J = 6.9 Hz, 12H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 146.7, 143.1, 142.5, 140.7, 130.4, 123.9, 123.6, 83.4, 52.2, 52.0, 27.9, 27.4, 24.8, 24.2, 24.1; IR (KBr) 3356, 2961, 1604, 1459, 1374, 1312, 1194 cm<sup>-1</sup>. Anal. Calcd for C<sub>32</sub>H<sub>51</sub>BN<sub>2</sub>O<sub>2</sub>: C, 75.87; H, 10.15; N, 5.53. Found: C, 75.89; H, 10.23; N, 5.47.

Compound 13. A mixture of 12 (217 mg, 0.50 mmol), 5 (279 mg, 0.55 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (58 mg, 0.050 mmol), K<sub>2</sub>CO<sub>3</sub> (83 mg, 0.60 mmol), DME (3.6 mL), and water (1.2 mL) was heated at 100 °C for 68 h. Water (20 mL) and diethyl ether (10 mL) were added. The organic layer was separated, and the aqueous layer was extracted with diethyl ether. The combined organic layer was dried over MgSO<sub>4</sub>, and the filtrate was concentrated. The crude product was purified by column chromatography (silica gel, hexane/AcOEt (4:1)) to afford 13 (312 mg, 85%) as colorless solid: mp 75.0-77.0 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) 7.49 (d, J = 8.4 Hz, 2H), 7.44-7.42 (m, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.20-7.12 (m, 6H),7.08-7.07 (m, 3H), 4.34 (t, J = 9.6 Hz, 2H), 3.98 (t, J = 9.6 Hz, 2H), 3.43 (septet, J = 6.6 Hz, 2H), 3.31 (septet, J = 6.6 Hz, 2H), 3.24 (t, J = 6.6 Hz, 2H), 3.19 (t, J = 6.6 Hz, 2H), 1.72 (s, 6H), 1.28(d, J = 6.6 Hz, 12H), 1.07 (d, J = 7.2 Hz, 12H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) 164.6, 148.3, 148.0, 143.6, 142.6, 142.5, 142.3, 140.6, 133.7, 131.74, 131.70, 130.8, 129.2, 129.0, 128.6, 127.4, 125.6, 125.2, 125.0, 124.1, 123.62, 123.57, 123.1, 122.9, 67.3, 54.9, 52.9, 52.1, 34.8, 31.7, 27.8, 27.7, 24.3, 24.1, 24.0; IR (KBr) 2960, 1645, 1428, 1399,  $1228 \text{ cm}^{-1}$ . Anal. Calcd for  $C_{50}H_{59}N_3O_2$ : C, 81.81; H, 8.10; N, 5.72. Found: C, 81.86; H, 8.22; N, 5.58.

Imidazolinium Salt 14. To a solution of 13 (220 mg, 0.30 mmol) in HC(OEt)<sub>3</sub> (6 mL) was added NH<sub>4</sub>Cl (18 mg, 0.33 mmol), and the mixture was heated at 120 °C for 20 h. All volatiles was removed under reduced pressure, and CH2Cl2 (10 mL) and 5% aqueous NaHCO<sub>3</sub> (10 mL) were added to the residue. The organic layer was separated, and the aqueous layer was extracted with  $CH_2Cl_2$ . The combined organic layer was dried over MgSO<sub>4</sub>, and the filtrate was concentrated. The product was purified by recrystallization from  $CH_2Cl_2$ /diethyl ether to afford 14 (194 mg, 83%) as colorless powder: mp 241.0-242.0 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 9.62 (s, 1H), 7.53-7.44 (m, 3H), 7.35-7.31 (m, 4H), 7.22-7.14 (m, 8H), 4.88 (s, 4H), 3.95 (t, J = 9.6 Hz, 2H), 3.09 (septet, J = 6.6 Hz, 2H), 2.98 (septet, J = 6.6 Hz, 2H), 2.47 (t, J = 9.6 Hz, 2H), 1.42 (d, J = 1.006.6 Hz, 6H), 1.35 (d, J = 6.6 Hz, 6H), 1.23 (d, J = 6.9 Hz, 6H), 0.90(d, J = 6.9 Hz, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 165.5, 160.2, 148.3, 147.9, 146.7, 145.7, 141.6, 140.9, 132.3, 131.5, 130.5, 129.5, 129.3, 129.2, 129.0, 128.9, 127.7, 127.0, 126.4, 125.5, 125.0, 124.9, 123.7, 123.6, 67.4, 55.8, 55.2, 52.3, 34.9, 30.9, 29.1, 25.3, 25.0, 23.4, 23.3; IR (KBr) 3397, 2964, 1632, 1431, 1399, 1262 cm<sup>-1</sup>; HR-MS (FAB) calcd for  $C_{51}H_{58}N_3O_2$  ([M - Cl]<sup>+</sup>) 744.4529, found 744.4528

AgCl Complex 15-Cl. A mixture of 14 (78 mg, 0.1 mmol) and Ag<sub>2</sub>O (14 mg, 0.06 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was stirred for 21 h at room temperature. The resulting precipitate was filtrated off, and the filtrate was concentrated. Ag complex 15-Cl was obtained (89 mg, quant) as a colorless solid and used without further purification. Suitable crystals for the X-ray crystal structural analysis were obtained by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/diethyl ether: mp 295.0-296.3 °C; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) 7.51-7.45 (m, 4H), 7.38 (t, J = 7.2 Hz, 1H), 7.33 (dd, J = 7.8, 1.8 Hz, 1H), 7.30 (d, J =8.4 Hz, 2H), 7.23-7.14 (m, 5H), 7.15-7.12 (m, 2H), 4.34 (t, J =9.6 Hz, 2H), 4.14-4.11 (m, 2H), 4.04-4.00 (m, 2H), 3.94 (t, J = 9.6 Hz, 2H), 3.04 (septet, J = 7.2 Hz, 2H), 2.93 (septet, J = 7.2 Hz, 2H), 1.74 (s, 6H), 1.34 (d, J = 7.2 Hz, 6H), 1.32 (d, J = 7.2 Hz, 6H), 1.27 (d, J = 6.6 Hz, 6H), 1.01 (d, J = 6.6 Hz, 6H); <sup>13</sup>C NMR  $(150 \text{ MHz}, \text{CDCl}_3) 207.4 (\text{dd}, J_{\text{C}-\text{Ag}} = 259, 223 \text{ Hz}), 164.4, 147.9,$ 147.5, 146.5, 145.8, 141.4, 139.5, 134.6, 133.3, 131.7, 130.6, 130.2, 130.0, 129.5, 129.39, 129.37, 128.1, 127.1, 126.0, 125.7, 125.2, 125.1, 124.6, 123.27, 123.26, 67.3, 54.9, 54.5 (d,  ${}^{3}J_{C-Ag} = 8.8$  Hz), 53.8 (d,  ${}^{3}J_{C-Ag} = 8.8$  Hz), 34.7, 31.8, 28.79, 28.76, 25.4, 24.0, 23.5; IR (KBr) 2962, 1646, 1491, 1397, 1364, 1273, 1219 cm<sup>-1</sup>; HR-MS (ESI) calcd 852.3503 ([M – CI]<sup>+</sup>), found 852.3487. Anal. Calcd for C<sub>51</sub>H<sub>57</sub>AgClN<sub>3</sub>O<sub>2</sub>: C, 69.03; H, 6.47; N, 4.74. Found: C, 69.03; H, 6.79: N. 4.32.

AgPF<sub>6</sub> Complex 15-PF<sub>6</sub>. To a solution of 15-Cl (89 mg, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added an excess amount of KPF<sub>6</sub> and water (3 mL), and the biphasic solution was stirred for 6 h. The organic layer was separated and dried over MgSO<sub>4</sub>. The filtrate was concentrated to afford 15-PF<sub>6</sub> (100 mg, quant) as a colorless solid. Suitable crystals for an X-ray structural analysis were obtained by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane: mp 195.0-196.0 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 7.52-7.43 (m, 7H), 7.35 (s, 2H), 7.31 (d, J = 7.8 Hz, 2H), 7.22-7.10 (m, 4H), 4.60 (t, J = 9.9 Hz, 2H), 4.23(br m, 4H), 3.59 (t, J = 9.9 Hz, 2H), 3.16-3.03 (m, 4H), 1.73 (s, 6H), 1.36 (d, J = 6.6 Hz, 6H), 1.34 (d, J = 6.3 Hz, 6H), 1.32 (d, J = 6.9 Hz, 6H), 1.04 (d, J = 6.9 Hz, 6H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) 204.0 (dd,  $J_{C-Ag} = 265.8$ , 227.1 Hz), 171.4 (br), 148.6, 147.9, 146.9, 146.5, 143.2, 140.6, 134.3, 133.3, 132.4, 131.5, 130.5, 130.1, 130.0, 129.8, 127.5, 126.7, 126.1, 125.0, 124.8, 123.8, 123.6, 122.8, 69.8, 54.9 (d,  ${}^{3}J_{C-Ag} = 8.8$  Hz), 54.0, 53.7 (d,  ${}^{3}J_{C-Ag} = 8.8$  Hz), 34.8, 31.1, 28.84, 28.78, 25.5, 25.4, 24.0, 23.6; IR (KBr) 2963, 1634, 1497, 1461, 1400, 1271, 1220, 1109 cm<sup>-1</sup>. Anal. Calcd for C<sub>51</sub>H<sub>57</sub>AgF<sub>6</sub>N<sub>3</sub>O<sub>2</sub>P: C, 61.45; H, 5.76; N, 4.22. Found: C, 61.18; H, 5.90; N, 4.13.

**Pd Complex 16.** A suspension of **15-Cl** (89 mg, 0.10 mmol) and Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> (42 mg, 0.11 mmol) in 1,4-dioxane (3 mL) was heated at 100 °C for 20 h. The resulting precipitate was filtrated off, and the filtrate was concentrated. The product was purified by column chromatography (silica gel, Hex/AcOEt (5:1)) to afford **16** (77 mg, 84%) as a yellow powder. Suitable crystals

for an X-ray structure analysis were obtained by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/diethyl ether: mp 218.3–218.7 °C; <sup>1</sup>H NMR  $(300 \text{ MHz}, \text{CDCl}_3) 8.16 \text{ (d}, J = 8.4 \text{ Hz}, 2\text{H}), 7.52-7.41 \text{ (m}, 7\text{H}),$ 7.32-7.20 (m, 5H), 7.16 (t, J = 7.5 Hz, 1H), 4.30 (t, J = 9.6 Hz,2H), 4.01 (m, 4H), 3.87 (t, J = 9.9 Hz, 2H), 3.64 (septet, J = 6.6Hz, 2H), 3.53 (t, J = 6.6 Hz, 2H), 1.74 (s, 6H), 1.58 (d, J = 6.6 Hz, 6H), 1.25 (d, J = 6.9 Hz, 6H), 1.21 (d, J = 6.9 Hz, 6H), 1.18 (d, J = 6.6 Hz, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 188.0, 166.6, 149.0, 148.4, 147.8, 147.5, 140.9, 139.3, 135.1, 135.0, 132.3, 131.8, 130.8, 129.8, 129.6, 129.4, 128.9, 127.7, 126.4, 125.1, 124.43, 124..37, 124.2, 123.5, 123.2, 67.9, 53.9, 53.8, 53.6, 34.9, 34.8, 30.8, 28.7, 28.6, 26.8, 26.6, 24.1, 23.9; IR (KBr) 2961, 1638, 1455, 1398, 1266, 1217, 1103 cm<sup>-1</sup>; HR-MS (ESI) calcd 944.2757 ([M + Na]<sup>+</sup>), 884.3174 ([M - Cl]<sup>+</sup>), found 944.2700, 884.3125. Anal. Calcd for C<sub>51</sub>H<sub>57</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>2</sub>Pd: C, 66.48; H, 6.24; N, 4.56. Found: C, 66.70; H, 6.25; N, 4.53.

Compound 18. A mixture of 11 (217 mg, 0.50 mmol), 17 (161 mg, 0.6 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (58 mg, 0.050 mmol), Na<sub>2</sub>CO<sub>3</sub> (128 mg, 0.125 mmol), HN(CH2CH2OH)2 (62 µL, 0.65 mmol), DME (1.5 mL), and water (0.5 mL) was heated at 100  $^{\circ}$ C for 15 h. H2O (10 mL) and CH2Cl2 (10 mL) were added. The organic layer was separated, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was dried over MgSO<sub>4</sub>, and the filtrate was concentrated. The product was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/MeOH (25:1)) to afford **18** (138 mg, 55%) as a colorless powder: mp 208.0-209.0 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 7.89 (s, 1H), 7.68 (d, J = 8.4 Hz, 2H), 7.48-7.44 (m, 2H), 7.33-7.29 (m, 4H), 7.20-7.12 (m, 4H), 7.07 (d, J = 8.7 Hz, 2H), 4.37 (t, J = 9.3 Hz, 2H), 4.01 (t, J =9.3 Hz, 2H), 1.71 (s, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 164.1, 147.84, 147.76, 140.8, 136.7, 135.7, 135.5, 131.3, 131.2, 130.8, 129.8, 129.6, 129.4, 128.6, 128.4, 127.5, 125.9, 125.2, 125.2, 123.3, 123.2, 121.8, 120.4, 118.6, 67.6, 54.8, 34.8, 31.4; IR (KBr) 2969, 1647, 1522, 1433, 1400, 1235, 1072 cm<sup>-1</sup>. Anal. Calcd for C33H27N3O2: C, 79.66; H, 5.47; N, 8.44. Found: C, 79.40; H, 5.55; N, 8.39.

Ag Complex 19. To a solution of 18 (480 mg, 0.964 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) was added MeI (2.5 mL), and the mixture was stirred at room temperature for 16 h. All volatiles were removed under reduced pressure. The residue was dissolved with CH2Cl2 (3 mL), and KPF<sub>6</sub> (1.20 g, 6.52 mmol) in H<sub>2</sub>O (2 mL) was added. After being stirred for 8 h at room temperature, the mixture was filtered on Celite, washed with H2O and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated. The residue was mixed with Ag<sub>2</sub>O (156 mg, 0.672 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL), and the mixture was stirred at room temperature for 18 h. The precipitate was removed by filtration on Celite and evaporated. The residue was dissolved with CH<sub>2</sub>Cl<sub>2</sub> (5 mL), and KPF<sub>6</sub> (1.20 g, 6.52 mmol) in H<sub>2</sub>O (2 mL) was added. After stirring for 6 h at room temperature, the solution was washed with H<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated. The crude product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/ diethyl ether, and a pale pink powder was obtained (291 mg, 39%): mp 291–293 °C; <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 7.84 (d,

 $J = 8.3 \text{ Hz}, 2\text{H}, 7.68 \text{ (d, } J = 8.3 \text{ Hz}, 2\text{H}), 7.64 \text{ (d, } J = 8.7 \text{ Hz}, 2\text{H}), 7.57 \text{ (dd, } J = 7.6, 1.5 \text{ Hz}, 1\text{H}), 7.56 \text{ (dd, } J = 7.6, 1.8 \text{ Hz}, 1\text{H}), 7.49 \text{ (d, } J = 6.4 \text{ Hz}, 2\text{H}), 7.32-7.34 \text{ (m, 2H)}, 7.31 \text{ (dd, } J = 7.6, 1.9 \text{ Hz}, 1\text{H}), 7.243 \text{ (dd, } J = 7.6, 7.5 \text{ Hz}, 1\text{H}), 7.235 \text{ (dd, } J = 7.6, 7.6 \text{ Hz}, 1\text{H}), 7.18 \text{ (dd, } J = 7.6, 1.9 \text{ Hz}, 1\text{H}), 4.79 \text{ (t, } J = 9.8 \text{ Hz}, 2\text{H}), 4.35 \text{ (t, } J = 9.8 \text{ Hz}, 2\text{H}), 4.05 \text{ (s, 3H)}, 1.74 \text{ (s, 6H)}; ^{13}\text{C}$ NMR (150 MHz, CD<sub>2</sub>Cl<sub>2</sub>) 171,7, 148.5, 148.1, 148.1, 143.9, 139.3, 132.0, 131.9, 131.8, 131.1, 130.5, 128.7, 128.5, 127.6, 127.2, 126.6, 124.9, 124.3, 124.2, 124.1, 124.03, 123.95, 123.9, 70.4, 55.5, 40.0, 35.1, 32.4; IR (KBr) 3436, 1653, 1429, 1399, 1212, 1106, 846, 752, 557, 412 \text{ cm}^{-1}; \text{HR-MS} (ESI) calcd 618.1311 ([M - PF<sub>6</sub>]<sup>+</sup>), found 618.1305. Anal. Calcd for C<sub>34</sub>H<sub>29</sub>AgF<sub>6</sub>N<sub>3</sub>O<sub>2</sub>P: C, 53.42; H, 3.82; N, 5.50. Found: C, 53.47; H, 4.04; N, 5.50.

Pd Complex 20. A mixture of silver complex 19 (207 mg, 0.27 mmol), Pd(PhCN)<sub>2</sub>Cl<sub>2</sub> (114 mg, 0.297 mmol), and Et<sub>4</sub>NCl (49 mg, 0.296 mmol) in 1,2-dichloroethane (5 mL) was stirred at 50 °C for 24 h. The resulting precipitate of AgCl was removed by filtration, and the filtrate was washed with brine. The organic layer was dried over MgSO<sub>4</sub>, and the filtrate was concentrated. The product was purified by column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>/MeOH (100:1)) to afford 20 (74 mg, 40%). A suitable crystal for an X-ray structure analysis were obtained by recrystallization from 1,4-dioxane/hexane: mp > 300 °C; <sup>1</sup>H NMR  $(400 \text{ MHz}, \text{CDCl}_3) 8.40 \text{ (d}, J = 8.4 \text{ Hz}, 2\text{H}), 7.86 \text{ (d}, J = 8.4 \text{ Hz},$ 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.51-7.48 (m, 2H), 7.30 (dd, J = 9.6, 1.6 Hz, 1H), 7.21–7.15 (m, 3H), 7.08 (d, J = 2.0 Hz, 1H), 7.04 (d, J = 2.0 Hz, 1H), 4.56 (t, J = 10.4 Hz, 2H), 4.37–4.32 (m, 5H), 1.73 (s, 6H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) 167.3, 152.2, 148.3, 147.9, 141.5, 139.0, 138.3, 131.44, 131.38, 131.1, 130.4, 129.8, 129.5, 128.8, 127.8, 127.8, 125.9, 125.7, 125.4, 124.2, 123.7, 123.6, 123.5, 123.1, 68.1, 54.2, 38.2, 34.6, 31.7; IR (KBr) 2923, 1648, 1432, 1401, 1220, 1103  $cm^{-}$ <sup>1</sup>; HR-MS (ESI) calcd 652.0987 ([M – Cl]<sup>+</sup>), found 652.0994. Anal. Calcd for C<sub>34</sub>H<sub>29</sub>Cl<sub>2</sub>N<sub>3</sub>O<sub>2</sub>Pd: C, 59.27; H, 4.24; N, 6.10. Found: C, 59.04; H, 4.32; N, 5.96.

General Procedure for X-ray Structure Analysis. X-ray diffraction data of the crystals were collected on a CCD diffractometer with graphite-monochromated Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation. Data collections were carried out at low temperature (90–150 K) using liquid nitrogen. The crystal structure was solved by direct methods using SHELXS-97 and refined by fullmatrix least-squares with SHELXL-97.<sup>17</sup> All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included at their calculated positions.

Supporting Information Available: An X-ray crystallographic information file containing full details of the structural analysis of complexes 15-Cl, 15-PF<sub>6</sub>, 16, and 20. Table of crystallographic detail (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

<sup>(17)</sup> A short history of SHELX. Sheldrick, G. M. Acta Crystallogr. 2008, A64, 112–122.