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Synthesis and Reactions of Pd^{II} Complexes with Aryl, Aroyl, and Iminoaroyl Ligands – Insertion of CO and RNC into the Pd–Ar Bond and Intermolecular Coupling of the Ligands

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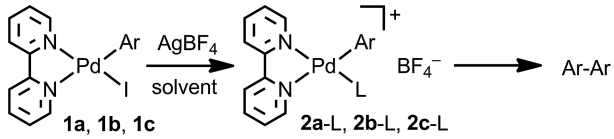
Keywords: Palladium / Transmetalation / C–C formation / Insertion / Isocyanides / Biaryls

The arylpalladium(II) complexes [PdIAr(bpy)] (Ar = Ph, C_6H_3-3,5-Me_2, C_6H_4-4-OMe, C_6H_4-2-OMe, C_6H_4-4-C_6H_4-4-I, 1-naphthyl; bpy = 2,2′-bipyridine) undergo insertion of CO and CNR (R = *t*Bu, C_6H_3-2,6-Me_2) into the Pd–aryl bond to produce [PdI(COAr)(bpy)] and [PdI{C(=N–R)Ar}(bpy)]. The dinuclear complex [C_6H_3-3,5-{$(OCH_2CH_2)_2C_6H_4$-3-PdI(bpy)}$_2$] is synthesized by the oxidative addition reaction of 1,3-bis[(3-iodophenyl)-1,4,7-trioxaheptyl]benzene to [Pd(dba)$_2$] (dba = dibenzylideneacetone). The addition of $AgBF_4$ to the arylpalladium(II) complexes [PdIAr(bpy)] (Ar = C_6H_4-4-OMe, C_6H_4-2-OMe, 1-naphthyl) produces the intermolecular coupling products of the aryl ligands, Ar–Ar. The reactions of $AgBF_4$ with the aroylpalladium(II) complexes [PdI(COAr)(bpy)] (Ar = C_6H_3-3,5-Me_2, C_6H_4-2-OMe) result in decarbonylation and intermolecular coupling of the ligands to yield the diarylketones. The iminoaroylpalladium(II) complex [PdI{C(=N*t*Bu)C_6H_3-3,5-Me_2}(bpy)] undergoes hydrolysis of the ligand to yield *t*BuNHCO(C_6H_3-3,5-Me_2). The addition of $AgBF_4$ to the dinuclear complex [C_6H_3-3,5-{$(OCH_2CH_2)_2$-C_6H_4-3-PdI(bpy)}$_2$] yields a mixture of the cyclic oligomers *cyclo*-[C_6H_3-3,5-{$(OCH_2CH_2)_2C_6H_4$-3-}$_2$]$_n$ (n = 1–4) by inter- and intramolecular coupling of the aryl ligands.

Introduction

Aryl(halide)palladium(II) complexes, [PdXAr(L)$_2$] (Ar = aryl, X = halide ligand, L = supporting ligand),[1,2] are regarded as the intermediates of cross-coupling reactions catalyzed by Pd complexes.[3,4] Homocoupling reactions of aryl halides promoted by Pd complexes also involve aryl(halide)palladium complexes as intermediates.[5–9] The homocoupling reactions of ArX involve disproportionation reactions of the arylpalladium(II) complexes to form di(aryl)palladium complexes and subsequent reductive elimination of the biaryl.[6–9] Arylpalladium(II) complexes react with small unsaturated molecules such as CO, isocyanide, and alkynes to form the corresponding aroyl-, iminoaroyl-, and benzylidenepalladium(II) complexes.[10–13] These reactions are involved in the carbonylation reactions of aryl halides[14] and the polymerizations of isocyanides catalyzed by Pd complexes.[15]

We reported that the arylpalladium(II) complexes [PdIAr(bpy)] [Ar = Ph (**1a**), C_6H_3-3,5-Me_2 (**1b**), and C_6H_3-3,5-$(CF_3)_2$ (**1c**); bpy = 2,2′-bipyridine] react with $AgBF_4$ to form the corresponding biaryls via the cationic intermediates [PdAr(L)(bpy)][BF_4] (**2a**-L to **2c**-L, L = solvent; Scheme 1).[7] The analogous cyclizative coupling reactions of the dinuclear palladium(II) complexes [{(bpy)(I)Pd(C_6H_4-3-{OCH_2CH_2}$_{0.5n+0.5}$)}$_2$O] and [{(bpy)(I)Pd(COC_6H_4-3-{OCH_2CH_2}$_{0.5n+0.5}$)}$_2$O] (n = 3, 5) produce cyclophanes.[8] In this paper, we report details of the reactions of aryl-, aroyl-, and iminoaroyl(iodido)palladium(II) complexes and elimination of the organic ligands by inter- and intramolecular coupling.



Ar = Ph (**1a**, **2a**), C_6H_3-3,5-Me_2 (**1b**, **2b**), C_6H_3-3,5-$(CF_3)_2$ (**1c**, **2c**)

Scheme 1. Reaction of $AgBF_4$ with [PdI(Ar)(bpy)] complexes **1a**–**1c**.

Results and Discussion

Synthesis of Aryl-, Aroyl-, and Iminoaroyl Palladium(II) Complexes

The new aryl(iodido)palladium(II) complexes **1d**–**1g** and the dinuclear Pd^{II} complex **1h** used in this study are summa-

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rized in Figure 1. The complexes were prepared in isolated yields of 6–39% by the oxidative addition of iodoarene to [Pd(dba)$_2$] {or [Pd$_2$(dba)$_3$CHCl$_3$], dba = dibenzylideneacetone} in the presence of 2,2′-bipyridine according to the method previously reported or its modification.[2b,7,8]

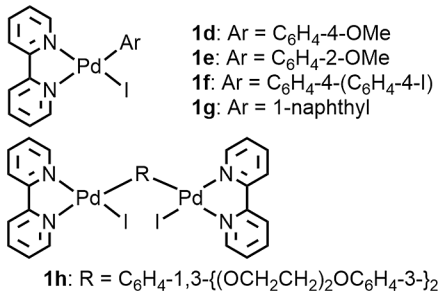
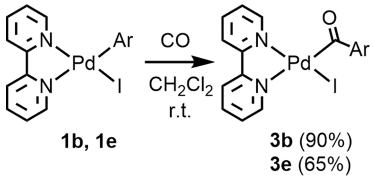
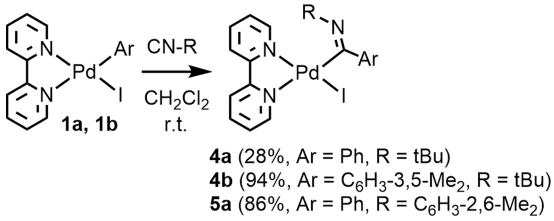


Figure 1. Palladium(II) complexes **1d**–**1h**.

The reactions of CO (1 atm) with [PdIAr(bpy)] [Ar = C_6H_3-3,5-Me_2 (**1b**), C_6H_4-2-OMe (**1e**)] form [PdI(COAr)(bpy)] [**3b** (90%), **3e** (65%), Equation (1)], and the insertion reactions of isocyanide CNR (R = *t*Bu, C_6H_3-2,6-Me_2) with [PdIAr(bpy)] [Ar = Ph (**1a**), C_6H_3-3,5-Me_2 (**1b**)] yield the iminoaroyl complexes [PdI{C(=NR)Ar}(bpy)] [**4a** (28%), **4b** (94%), **5a** (86%), Equation (2)].



(1)



(2)

These complexes **1d**–**1h**, **3b**, **3e**, **4a**, **4b**, and **5a**, were characterized by ^{1}H and ^{13}C{^{1}H} NMR and IR spectroscopy as well as by elemental analysis and X-ray crystallography for **1d**, **1e**, **1f**, **3b**, **4a**, and **5a**. Single crystals of **1e**, **1f**, and **3b** were obtained as solvates with the recrystallization solvent **1e**$_3$·CH_2Cl_2, **1f**·CH_2Cl_2, and **3b**·$CHCl_3$, respectively. The molecular structures of **1e**, **3b**, **4a**, and **5a** with square-planar coordination geometries around the Pd^{II} centers are shown in Figure 2. The Pd–C bond lengths of **1d** [1.987(7) Å], **1e** [1.99 Å (average)], **1f** [2.01(1) Å], **4b** [1.983(8) Å], and **5a** [1.985(4) Å] are in a similar range. The Pd atom and *t*Bu group of **4a** (and the C_6H_3-2,6-Me_2 group of **5a**) occupy *syn* positions of the C=N bond. The C=O bond length of **3b** [1.18(2) Å] and the C=N bond lengths of **4b** [1.265(4) Å] and of **5a** [1.27(1) Å] are similar to those of previously reported aroyl- and iminoaroyl palladium(II) complexes.[11,16] The IR spectra of **3b**, **3e**, **4a**, **4b**, and **5a** contain characteristic absorption peaks assigned to ν(C=O) [$\tilde{\nu}$ = 1644 (**3b**), 1667 (**3e**) cm^{-1}][17] and ν(C=N) [$\tilde{\nu}$ = 1619 (**4a**), 1609 (**4b**), 1619 (**5a**) cm^{-1}] vibrations. The ^{13}C{^{1}H} NMR spectra show the peaks for the carbonyl carbon atoms of **3b** (δ = 224.8 ppm) and the imino carbon atoms of **4a** (δ = 171.4 ppm) and **5a** (δ = 178.8 ppm).

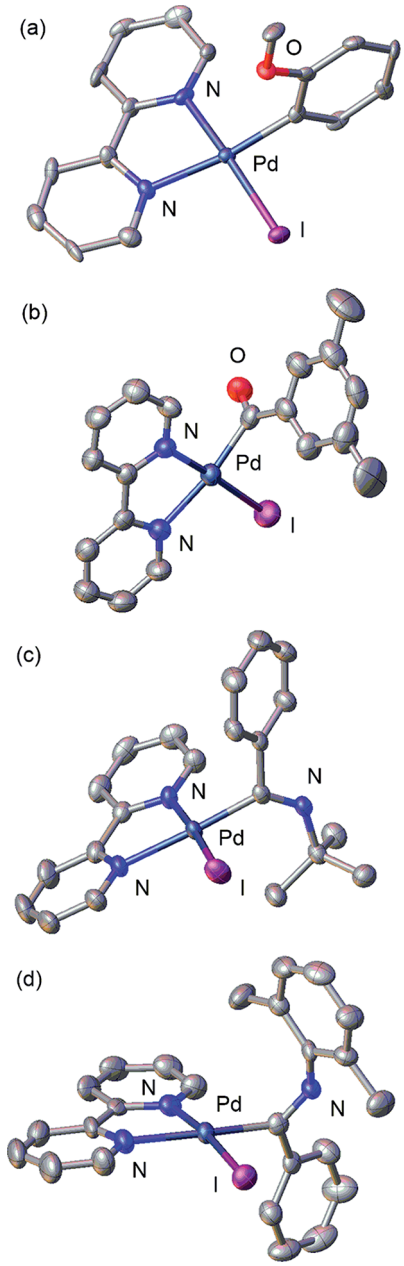
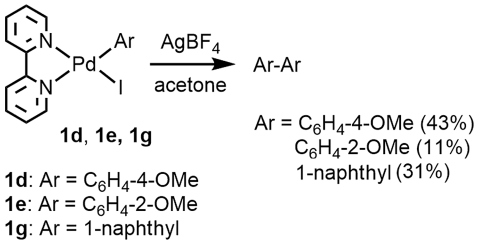


Figure 2. Crystal structures of (a) **1e**, (b) **3b**, (c) **4a**, and (d) **5a**.

Intermolecular Aryl Ligand Coupling Reactions of Arylpalladium(II) Complexes

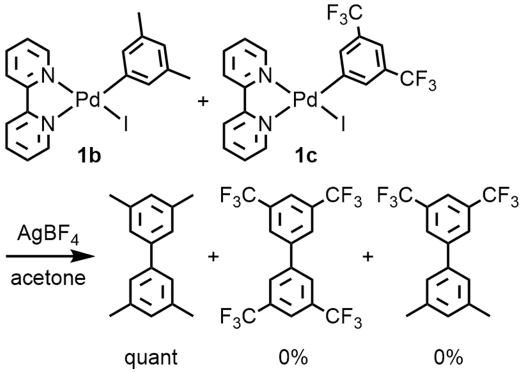
The dissolution of **1d** (0.21 mmol) and $AgBF_4$ (0.40 mmol) in acetone leads to the formation of 4,4′-di-

methoxybiphenyl (0.045 mmol, 43%) after 1 h [Equation (3)]. The reactions of the arylpalladium(II) complexes [PdIAr(bpy)] [Ar = C_6H_4-2-OMe (**1e**), 1-naphthyl (**1g**)] with $AgBF_4$ also result in intermolecular coupling of the aryl ligands to yield biaryls Ar–Ar (Ar = C_6H_4-2-OMe, 1-naphthyl). The lower yield of 2,2′-dimethoxybiphenyl (11%) than those of 4,4′-dimethoxybiphenyl (43%) and 1,1′-binaphthyl (31%) is ascribed to prevention of smooth transmetalation and/or reductive elimination because of the steric repulsion of the *ortho*-OMe group on the aryl group of **1e**. In these reactions, the formation of Pd metal as a black precipitate immediately after the addition of $AgBF_4$ was observed; this suggests that Pd^0 species form and aggregate at the end of the reactions. The following inter- and intramolecular coupling reactions also result in precipitation of Pd metal.



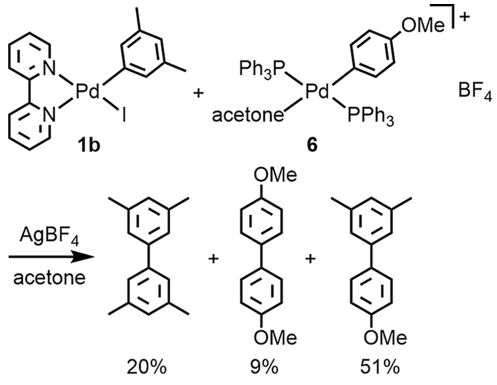
(3)

We compared the reactivity of the arylpalladium complexes with different aryl ligands. As shown in a previous report,[7] the palladium(II) complex **1b** with a 3,5-dimethylphenyl group shows a much higher reactivity than that of **1c** with a 3,5-bis(trifluoromethyl)phenyl ligand. A competition reaction was conducted as follows. The addition of $AgBF_4$ to a mixture of **1b** and **1c** yields 3,3′,5,5′-tetramethylbiphenyl, quantitatively. The formation of 3,3′,5,5′-tetrakis(trifluoromethyl)biphenyl and 3,5-bis(trifluoromethyl)-3′,5′-dimethylbiphenyl is not observed [Equation (4)]. These results suggest that the cationic complex [Pd{C_6H_3-3,5-$(CF_3)_2$}(acetone)(bpy)][BF_4] (**2c**-acetone) is stable and does not react with [Pd{C_6H_3-3,5-Me_2}(acetone)(bpy)][BF_4] (**2a**-acetone) to cause intermolecular coupling of the aryl ligands.



(4)

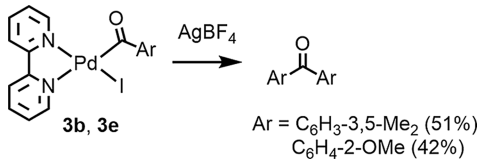
The reaction of $AgBF_4$ with a mixture of **1b** and [Pd(C_6H_4-4-OMe)(acetone)$(PPh_3)_2$][BF_4] (**6**) results in a mixture of 3,3′,5,5′-tetramethylbiphenyl (20%), 4,4′-dimethoxybiphenyl (9%), and 3,5-dimethyl-4′-methoxybiphenyl (51%) [Equation (5)]. The intermolecular transmetalation reactions of the aryl groups of [Pd(C_6H_3-3,5-Me_2)(acetone)(bpy)][BF_4] (**2b**-acetone) and **6** should occur during the reaction; therefore, the exchange of the aryl ligands of **2b**-acetone and **6** affords a mixture of [Pd(C_6H_4-4-OMe)(acetone)(bpy)][BF_4] (**2d**-acetone) and [Pd(C_6H_3-3,5-Me_2)(acetone)$(PPh_3)_2$][BF_4]. The formation of 3,5-dimethyl-4′-methoxybiphenyl (51%) in a higher yield than that of 4,4′-dimethoxybiphenyl from the reaction of **1d** with $AgBF_4$ [43%, Equation (3)] indicates that smooth transmetalation of the 4-methoxyphenyl ligand yields [Pd(C_6H_3-3,5-Me_2)(C_6H_4-4-OMe)(bpy)].



(5)

Carbonylative Coupling Reactions of Aroylpalladium(II) Complexes

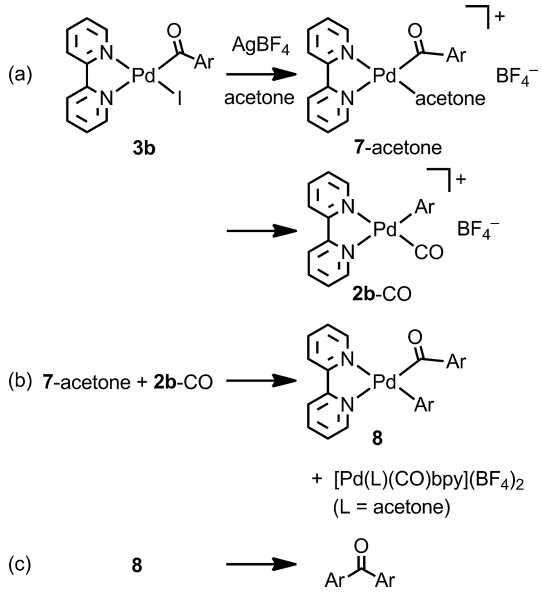
The reactions of CO with mono- and dinuclear acyl and aroyl organopalladium and -platinum complexes form ketones.[18] The reactions of $AgBF_4$ with the aroylpalladium(II) complexes [PdI(COAr)(bpy)] (**3b**, Ar = C_6H_3-3,5-Me_2; **3e**, Ar = C_6H_4-2-OMe) yield the diarylketones ArCOAr (51 and 42%) rather than the diketones ArCOCOAr [Equation (6)].[14]



(6)

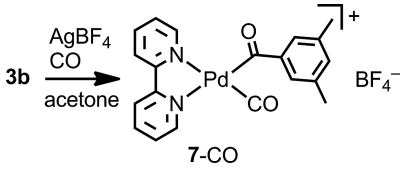
The pathway for the formation of the diarylketone from the reaction of $AgBF_4$ with **3b** is shown in Scheme 2. The reaction of $AgBF_4$ with **3b** affords [Pd(COAr)(acetone)(bpy)][BF_4] (**7**-acetone, Scheme 2, a). The decarbonylation of **7**-acetone yields the aryl complex [PdAr(CO)(bpy)][BF_4]

(**2b**-CO). The ligand exchange of **7**-acetone and **2b**-CO yields a mixture of [Pd(COAr)Ar(bpy)][BF_4] (**8**) and [Pd(acetone)(CO)(bpy)][BF_4]$_2$ (Scheme 2, b). The former product causes reductive elimination of the diarylketone (Scheme 2, c).



Scheme 2. A plausible mechanism for the reaction of $AgBF_4$ with **3b** to afford ArCOAr.

The reaction of $AgBF_4$ with **3b** under CO (1 atm) results in the formation of the cationic complex **7**-CO [Equation (7)]. The IR spectrum of **7**-CO exhibits a characteristic ν(CO) band for the carbonyl ligand [$\tilde{\nu}$ = 2149 cm^{-1}]. The $^{13}C\{^1H\}$ NMR spectrum of **7**-CO contains signals assigned to C=O (δ = 208.5 ppm) and C≡O groups (δ = 168.4 ppm, Figure 3). The peaks of the bipyridine carbon atoms [δ = 119.4 (3,3′), 123.6 (5,5′), 147.3 (4,4′), 151.4 (2,2′) ppm] were observed as a single set of four broad signals (Figure 3). The ^1H NMR spectrum of **7**-CO shows four signals for the bipyridine hydrogen atoms [δ = 7.87 (5,5′), 8.45 (4,4′), 8.58 (6,6′), 8.75 (3,3′) ppm] at room temperature (Figure 4), and the signals for the 5,5′ and 6,6′ protons are observed as split signals at –30 °C [δ = 7.84 and 7.93 (5,5′), 8.19 and 8.96 (6,6′) ppm]. Thus, the migration of the aryl ligand of **7**-CO in solution (Scheme 3) makes the two pyridyl groups of the bipyridine ligand magnetically equivalent at room temperature.[19] The cleavage and closure of one Pd–N bond also accounts for the NMR spectra of **7**-CO.[20]



(7)

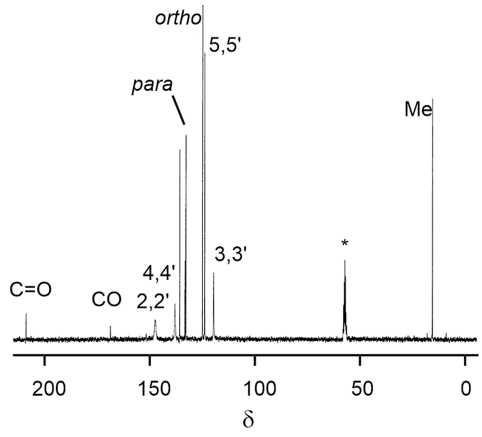


Figure 3. $^{13}C\{^1H\}$ NMR spectrum of **7**-CO (100 MHz, room temp., CD_3NO_2). The asterisk indicates the resonance from the solvent carbon atoms.

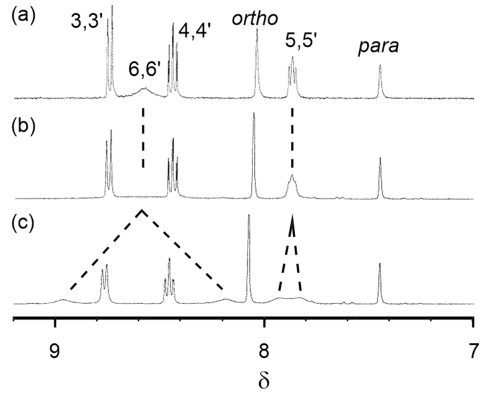
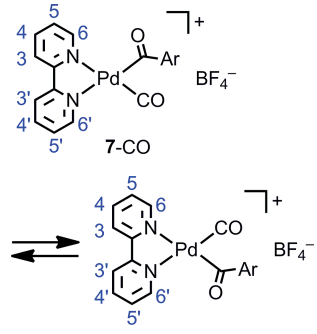


Figure 4. ^1H NMR spectrum of **7**-CO (400 MHz, [D_6]acetone) at (a) room temp., (b) 0 °C, and (c) –30 °C.

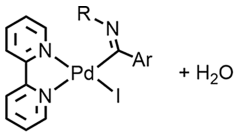


Scheme 3. A plausible isomerization of **7**-CO involving migration of an aryl group.

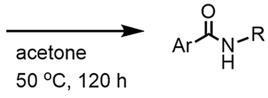
Hydrolysis of Iminoaryl Complex

The reaction of H_2O with the iminoaroylpalladium(II) complex [PdI{C(=N*t*Bu)Ar}(bpy)] (**4b**, Ar = C_6H_3-3,5-Me_2) at 50 °C for 120 h yields *t*BuNHCO(C_6H_3-3,5-Me_2) in 21% yield [Equation (8)]. The reaction of **5a** and H_2O under similar conditions does not yield the corresponding amide (C_6H_3-2,6-Me_2)NHCOPh, but the starting complex was recovered. The formation of the amide *t*BuNHCO(C_6H_3-3,5-Me_2) would involves hydrolysis of the Pd–C

bond by addition of H_2O to the C=N bond.[21] The lower reactivity of **5a** than that of **4b** is ascribed to the steric hindrance of the 2,6-dimethyl groups of **5a**, which prevents the reaction with H_2O, and the electron-donation from the *t*Bu group of **4b** to the imine nitrogen atom enhances the smooth addition of H_2O to the C=N bond. The hydrolyses of the imino ligands of (iminoacyl)vanadium(III) and (2-alkenyl-1-imino)iron complexes have been reported.[22]



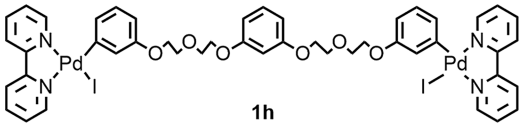
4b (Ar = C_6H_3-3,5-Me_2, R = tBu)
5a (Ar = Ph, R = C_6H_3-2,6-Me_2)



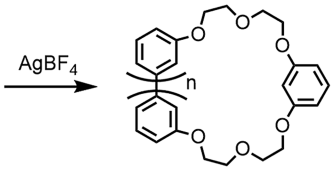
21% (Ar = C_6H_3-3,5-Me_2, R = tBu)
0% (Ar = Ph, R = C_6H_3-2,6-Me_2) (8)

Intramolecular Aryl Ligand Coupling Reactions of a Dinuclear Palladium(II) Complex

The reaction of excess $AgBF_4$ (0.24 mmol) with the dinuclear complex **1h** (0.081 mmol) yields cyclic ethylene glycols **9** (31%) by oligomerization of the bridging ligand [Equation (9)]. The ESI-MS spectra of **9** contain peaks at *m*/*z* = 459.16, 895.33, 1331.36, and 1768.75, which are assigned to *cyclo*-[C_6H_3-3,5-{$(OCH_2CH_2)_2$-C_6H_4–3-}$_2$]$_n$ (*n* = 1–4, respectively, detected as Na^+ adducts; Figure 5). The oligomerization reaction of **1h** involves inter- or intramolecular coupling reactions of the aryl ligands as a chain propagation reaction to afford the linear intermediate dinuclear complex **A** and the termination reaction to form complex **B** (Scheme 4). Reductive elimination from palladacycle **B** yields the cyclic oligomers.



1h



9 (n = 1, 2, 3, 4) (9)

Previously, we reported that the dinuclear palladium(II) complexes {[(bpy)(I)Pd{$C_6H_4(OCH_2CH_2)_n$}]$_2$O} (*n* = 2, 3), which have bridging ligands with long tethers, react with $AgBF_4$ to give the cyclization products *cyclo*-[C_6H_4-$(OCH_2CH_2)_n$]$_2$ (*n* = 2, 3), and the template effect of the Ag^+ ions enhances the cyclization.[8] The cyclizative oligomerization of **1h** is attributed to relatively weaker interactions between the Ag^+ ions and the bridging ligand of **1h** through the 1,3-phenylene unit, which accelerate the intermolecular coupling of the ligands.

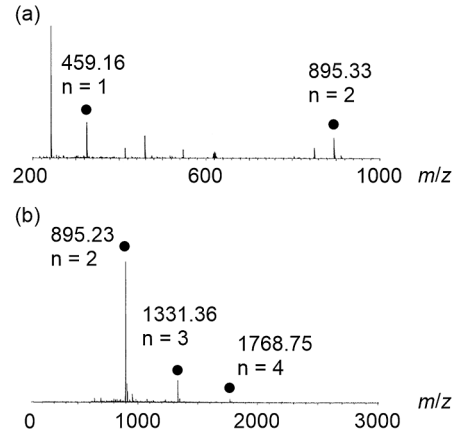
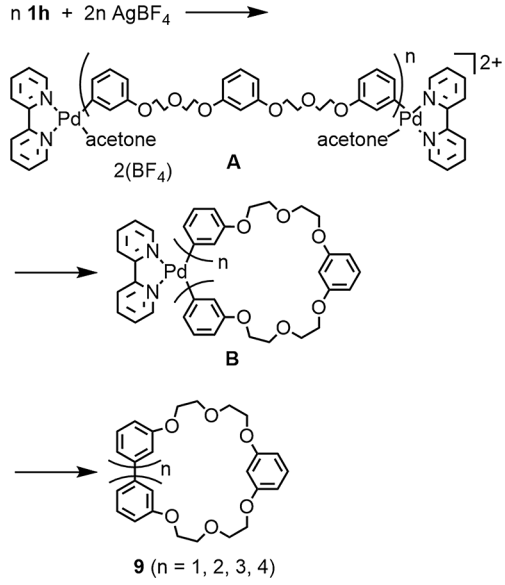


Figure 5. ESI-MS spectra of **9** (eluent; acetone). The spectra were obtained in (a) lower and (b) higher molecular weight mode.



Scheme 4. A plausible mechanism of the cyclization oligomerization of **1h** and $AgBF_4$.

Conclusions

We isolated aryl-, aroyl-, and iminoaroylpalladium(II) complexes with iodido and 2,2′-bipyridine (bpy) ligands and investigated their reactivity. The reactions of $AgBF_4$ with aryl(iodido)palladium(II) complexes yield biaryls, Ar–Ar. Intermolecular aryl ligand exchange reactions were noted through crossover experiments of the aryl ligands of the palladium(II) complexes. The coupling reactions of [PdI(COAr)(bpy)] yield ketones, ArCOAr, and the reactions are induced by the formation of cationic arylpalladium

complexes, $[Pd(COAr)(L)(bpy)]^+$, followed by decarbonylation reaction to give $[PdArCO(bpy)]^+$ and facile aryl ligand transfer between the metal centers. The iminoaroyl ligand of the palladium(II) complex [PdI{C(=NR)Ar}(bpy)] is eliminated by hydrolysis of the imino group as RNHCOAr. The aryl ligand coupling reaction was also applied to the cyclizative oligomerization reaction of a dinuclear palladium(II) complex. These reactions have a common cationic intermediate, which undergoes facile aryl ligand transfer. The Pd–bpy system in this study is less common than systems with phosphine ligands but will provide further insight into C–C bond-forming reactions.

Experimental Section

General: $[Pd(dba)_2]$[23] and [PdIAr(bpy)] (**1a–1c**)[2b,7] were prepared according to the previous reports. The other chemicals were commercially available. NMR spectra (^1H and $^{13}C\{^1H\}$) were recorded with MERCURY300 (Varian), EX-400 (JEOL), and Avance III-400 and -500 (Bruker) spectrometers. The ^1H chemical shifts were referenced to $CHCl_3$ (δ = 7.26 ppm), $CDHCl_2$ (δ = 5.32 ppm), and [D_5]acetone (δ = 2.04 ppm), and the ^{13}C chemical shifts were referenced to $CDCl_3$ (δ = 77.0 ppm), CD_2Cl_2 (δ = 53.1 ppm), and CD_3NO_2 (δ = 57.3 ppm) as internal standards. IR spectra were measured with FTIR-8100A (Shimadzu) and FTIR-4100 (JASCO) instruments. ESI-MS were obtained with a micrOTOF II (Bruker) spectrometer. GC–MS were performed with a QP-5000 mass spectrometer equipped with GC-17A (Shimadzu) chromatograph. Elemental analysis was performed with CHNS-932 (LECO) or MT-5 CHN (Yanaco) analyzers.

[PdI(C_6H_4-4-OMe)(bpy)] (1d): To a toluene (25 mL) solution of $[Pd(dba)_2]$ (1.39 g, 2.42 mmol) and bpy (487 mg, 3.12 mmol) was added IC_6H_4-4-OMe (576 mg, 2.46 mmol). The reaction mixture was stirred for 14 h at 50 °C, and the insoluble black solid was separated by filtration. The evaporation of the filtrate gave an orange solid. Reprecipitation of the crude product from CH_2Cl_2/Et_2O (3/100 mL) gave **1d** as a yellow powder (469 mg, 0.945 mmol, 39%). $C_{17}H_{15}IN_2OPd$ (496.62): calcd. C 41.11, H 3.04, N 5.64, I 25.55; found C 40.89, H 2.68, N 5.68, I 25.74. ^1H NMR (CD_2Cl_2, 400 MHz, room temp.): δ = 3.77 (s, 3 H, OMe), 6.73 (d, J = 9 Hz, 2 H, C_6H_4), 7.19 (d, J = 9 Hz, 2 H, C_6H_4), 7.38 (ddd, J = 7, 5, 1 Hz, 1 H, bpy), 7.56 (ddd, J = 7, 5, 1 Hz, 1 H, bpy), 7.71 (d, J = 6 Hz, 1 H, bpy), 8.01 (ddd, J = 8, 6, 2 Hz, 1 H, bpy), 8.03 (ddd, J = 8, 6, 2 Hz, 1 H, bpy), 8.10 (d, J = 8 Hz, 1 H, bpy), 8.10 (d, J = 8 Hz, 1 H, bpy), 9.58 (d, J = 6 Hz, 1 H, bpy) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, room temp.): δ = 55.3 (OMe), 113.6, 122.0, 122.3, 126.6, 127.0, 133.7, 136.6, 138.9, 138.9, 150.3, 152.8, 154.1, 156.0, 157.1 ppm.

[PdI(C_6H_4–2-OMe)(bpy)] (1e): Compound **1e** was prepared similarly to **1d**. The reaction of $[Pd(dba)_2]$ (987 mg, 1.72 mmol), bpy (353 mg, 2.26 mmol), and IC_6H_4-2-OMe (0.32 mL, 2.46 mmol) in toluene (25 mL) at 50 °C for 13 h yielded **1e** (219 mg, 0.442 mmol, 26%) as a yellow solid. The recrystallization of **1e** from CH_2Cl_2 yielded single crystals of the dichloromethane solvate **1e**$_3$·CH_2Cl_2. $C_{17}H_{15}IN_2OPd(CH_2Cl_2)_{0.33}$ (524.7): calcd. C 39.66, H 3.01, N 5.34, I 24.17; found C 39.96, H 2.78, N 5.43, I 23.88. ^1H NMR ($CDCl_3$, 400 MHz, room temp.): δ = 3.80 (s, 3 H, OMe), 6.69 (d, J = 8 Hz, 1 H), 6.77 (ddd, J = 7, 7, 1 Hz, 1 H), 7.01 (ddd, J = 8, 8, 1 Hz, 1 H), 7.32 (ddd, J = 7, 7, 1 Hz, 1 H), 7.42 (dd, J = 8, 1 Hz, 1 H), 7.53 (dd, J = 7, 7 Hz, 1 H), 7.71 (d, J = 6 Hz, 1 H), 7.95–8.07 (4 H), 9.71 (d, J = 5 Hz, 1 H, bpy) ppm. Selected $^{13}C\{^1H\}$ NMR spectroscopic data ($CDCl_3$, 100 MHz, room temp.): δ = 56.2 (OMe), 120.5, 121.3, 121.8, 124.5, 126.3, 126.7, 138.2, 138.4, 138.5, 150.4, 153.3 ppm. Only 12 signals were detected as the low solubility of **1e** resulted in a $^{13}C\{^1H\}$ NMR spectrum with a poor signal-to-noise ratio.

[PdI(C_6H_4-4-C_6H_4-4-I)(bpy)] (1f): Compound **1f** was prepared similarly to **1d**. The reaction of $[Pd_2(dba)_3CHCl_3]$ (313 mg, 0.30 mmol), bpy (123 mg, 0.79 mmol), and IC_6H_4-4-C_6H_4-4-I (245 mg, 0.60 mmol) in toluene (7.0 mL) at 50 °C for 18 h yielded **1f** (24 mg, 0.036 mmol, 6%) as a yellow solid. The recrystallization of **1f** from CH_2Cl_2 yielded single crystals of the dichloromethane solvate **1f**·CH_2Cl_2. $C_{22}H_{16}I_2N_2Pd(CH_2Cl_2)$ (753.5): calcd. C 36.66, H 2.41, N 3.72; found C 36.63, H 2.29, N 3.70. ^1H NMR (CD_2Cl_2, 400 MHz, room temp.): δ = 7.30 (d, J = 8 Hz, 2 H, C_6H_4), 7.37–7.42 (bpy, 3 H), 7.45 (d, J = 8 Hz, 2 H, C_6H_4), 7.59 (dd, J = 6, 7 Hz, 1 H, bpy), 7.75 (d, J = 8 Hz, 2 H, C_6H_4), 7.75 (d, J = 8 Hz, 1 H, bpy), 8.02 (d, J = 8 Hz, 1 H, C_6H_4), 8.05 (d, J = 8 Hz, 1 H, C_6H_4), 8.12 (d, J = 8 Hz, 2 H, bpy), 9.61 (d, J = 5 Hz, 1 H, bpy) ppm. Low solubility prevented $^{13}C\{^1H\}$ NMR spectroscopy measurement.

[PdI(1-naphthyl)(bpy)] (1g): Compound **1g** was prepared similarly to **1d**. The reaction of $[Pd(dba)_2]$ (348 mg, 0.61 mmol), bpy (124 mg, 0.79 mmol), and 1-iodonaphthalene (250 mg, 0.98 mmol) in toluene (6.0 mL) at 50 °C for 36 h yielded **1g** (69 mg, 0.13 mmol, 21%) as an orange solid. $C_{20}H_{15}IN_2Pd(H_2O)_{0.5}$ (525.7): calcd. C 45.70, H 3.07, N 5.33, I 24.14; found C 46.03, H 2.84, N 5.34, I 24.28. ^1H NMR (CD_2Cl_2, 400 MHz, room temp.): δ = 7.14 (ddd, J = 8, 6, 1 Hz, 1 H), 7.23–7.20 (2 H), 7.32 (ddd, J = 8, 7, 1 Hz, 1 H), 7.36 (ddd, J = 8, 7, 1 Hz, 1 H), 7.48 (d, J = 8 Hz, 1 H), 7.54 (d, J = 7 Hz, 1 H, 1 Hz), 7.63 (ddd, J = 7, 5, 1 Hz, 1 H), 7.70 (dd, J = 9, 1 Hz, 1 H), 7.94 (ddd, J = 8, 8, 2 Hz, 1 H, bpy), 8.07 (ddd, J = 8, 8, 2 Hz, 1 H, bpy), 8.09 (d, J = 8 Hz, 1 H, bpy), 8.13 (d, J = 8 Hz, 1 H, bpy), 8.80 (ddd, J = 5, 2, 1 Hz, 1 H, bpy), 9.69 (dd, J = 5, 1 Hz, 1 H, bpy) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, room temp.): δ = 122.0, 122.3, 123.3, 123.8, 124.9, 125.1, 126.6, 127.2, 127.7, 133.7, 133.8, 134.5, 138.9, 139.0, 139.8, 147.7, 150.1, 152.9, 154.2, 156.2 ppm.

HO(CH_2CH_2O)$_2$$C_6H_4$-3-I: A solution of HO($CH_2CH_2O$)$_2$Cl (1.90 mL, 17.8 mmol), HOC_6H_4-3-I (2.67 g, 12.1 mmol), and K_2CO_3 (3.37 g, 24.4 mmol) in *N*,*N*-dimethylformamide (DMF, 5.0 mL)was stirred at 100 °C for 15 h. The resulting solution was partitioned by the addition of water and Et_2O. The separated organic phase was dried with $MgSO_4$, filtered, and evaporated to yield HO(CH_2CH_2O)$_2$$C_6H_4$-3-I as a pale orange oil (2.85 g, 9.24 mmol, 76%). ^1H NMR ($CDCl_3$, 400 MHz, room temp.): δ = 3.67 (m, 2 H, CH_2), 3.76 (m, 2 H, CH_2), 3.85 (m, 2 H, CH_2), 4.11 (m, 2 H, CH_2), 6.88 (m, 1 H, C_6H_4), 6.99 (dd, J = 8, 8 Hz, 1 H, C_6H_4), 7.24–7.31 (m, 2 H, C_6H_4) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, room temp.): δ = 61.8 (CH_2), 67.6 (CH_2), 69.6 (CH_2), 72.6 (CH_2), 94.3 (C_6H_4), 114.4 (C_6H_4), 123.9 (C_6H_4), 130.2 (C_6H_4), 130.8 (C_6H_4), 159.3 (C_6H_4) ppm.

TsO(CH_2CH_2O)$_2$$C_6H_4$-3-I (Ts = –$SO_2C_6H_4$-4-Me): A CH_2Cl_2 (25 mL) solution of HO(CH_2CH_2O)$_2$$OC_6H_4$-3-I (4.21 g, 13.7 mmol), pyridine (4.0 mL, 50 mmol), and TsCl (4.91 g, 25.8 mmol) was stirred at room temp. for 15 h. The resulting solution was washed with brine and water, and the product was extracted with CH_2Cl_2. The separated organic phase was dried with $MgSO_4$, filtered, and evaporated to yield the crude product, which was purified by silica gel column chromatography (eluent: hexane/AcOEt 10:1–1:1) to yield TsO(CH_2CH_2O)$_2$$OC_6H_4$-3-I as an orange oil (3.34 g, 7.44 mmol, 54%). $C_{17}H_{19}IO_5S$ (462.30): calcd. C 44.17, H 4.14; found C 44.11, H 4.10. ^1H NMR ($CDCl_3$, 500 MHz, room

temp.): δ = 2.42 (s, 3 H, Me), 3.74–3.78 (m, 4 H, CH_2), 4.01 (m, 4 H, CH_2), 4.19 (m, 4 H, CH_2), 6.85 (ddd, J = 8, 3, 1 Hz, 1 H), 6.99 (dd, J = 8, 8 Hz, 1 H), 7.23 (dd, J = 2, 2 Hz, 1 H), 7.28–7.32 (3 H), 7.79 (d, J = 8 Hz, 2 H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz, room temp.): δ = 21.6 (CH_3), 67.5 (CH_2), 68.9 (CH_2), 69.2 (CH_2), 69.7 (CH_2), 94.3 (PhI), 114.2, 123.7, 128.0, 129.8, 130.1, 130.8, 132.9, 144.8, 159.2 ppm.

C_6H_4-1,3-{$(OCH_2CH_2)_2OC_6H_4$-3-I}$_2$: A DMF (30 mL) solution of $TsO(CH_2CH_2O)_2C_6H_4$-3-I (1.59 g, 3.4 mmol), C_6H_4-1,3-$(OH)_2$ (218 mg, 1.98 mmol), and Cs_2CO_3 (3.70 g, 11.3 mmol) was stirred at room temp. for 25 h. The resulting solution was washed with water, and the product was extracted with Et_2O. The separated organic phase was dried with $MgSO_4$, filtered, and evaporated to yield a crude solid, which was washed with hexane/AcOEt (3:1 v/v) to yield C_6H_4-1,3-{$(OCH_2CH_2)_2OC_6H_4$-3-I}$_2$ as a white powder (694 mg, 1.0 mmol, 59%). $C_{26}H_{28}I_2O_6$ (690.31): calcd. C 45.24, H 4.09, I 36.77; found C 45.09, H 3.98, I 36.46. ^1H NMR ($CDCl_3$, 400 MHz, room temp.): δ = 3.90 (m, 8 H, CH_2), 4.12 (m, 8 H, CH_2), 6.50–6.54 (3 H), 6.88 (ddd, J = 8, 2, 1 Hz, 2 H), 6.98 (dd, J = 8, 8 Hz, 2 H), 7.16 (dd, J = 8 Hz, 1 H), 7.26–7.30 (m, 4 H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, room temp.): δ = 67.5 (CH_2), 67.7 (CH_2), 69.8 (CH_2), 70.0 (CH_2), 94.3, 101.9, 107.3, 114.4, 124.0, 129.9, 130.1, 130.7, 159.3, 159.9 ppm.

[C_6H_4-1,3-{$(OCH_2CH_2)_2OC_6H_4$-3-PdI(bpy)}$_2$] (1h): Compound **1h** was prepared similarly to **1d**. The reaction of [$Pd_2(dba)_3CHCl_3$] (634 mg, 0.61 mmol), bpy (241 mg, 1.54 mmol), and C_6H_4-1,3-{$(OCH_2CH_2)_2OC_6H_4$-3-I}$_2$ (418 mg, 0.61 mmol) in toluene (25 mL) at 50 °C for 34 h yielded **1h** (110 mg, 0.090 mmol, 14%) as a yellow solid. $C_{46}H_{44}I_2N_4O_6Pd_2$ (1215.49): calcd. C 45.45, H 3.65, N 4.61, I 20.88; found C 45.91, H 3.63, N 4.14, I 20.81. ^1H NMR (CD_2Cl_2, 500 MHz, room temp.): δ = 3.85 (8 H, CH_2), 4.06–4.15 (8 H, CH_2), 6.44–6.53 (5 H), 6.90–6.98 (6 H), 7.11 (dd, J = 7, 7 Hz, 1 H), 7.32 (m, 2 H, bpy), 7.50–7.67 (4 H, bpy), 7.97–8.05 (ddd, 4 H, bpy), 8.05–8.11 (4 H, bpy), 9.55 (m, 2 H, bpy) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100 MHz, room temp.): δ = 67.4 (CH_2), 67.8 (CH_2), 69.9 (CH_2), 70.2 (CH_2), 101.6, 107.1, 109.6, 120.0, 122.3* (bpy), 122.4* (bpy), 126.7 (bpy), 126.9 (bpy), 127.2, 129.4, 130.0, 139.0* (2C, bpy), 147.9, 150.3* (bpy), 152.7* (bpy), 154.0* (bpy), 155.8* (bpy), 157.1, 160.2 ppm; the asterisks indicate the split signals.

[PdI(COC_6H_4–3,5-Me_2)(bpy)] (3b): To a CH_2Cl_2 (15 mL) solution of **1b** (1.29 g, 2.61 mmol), CO (1 atm) was introduced, and the solution was stirred for 3 h at room temperature. After filtration to remove a small amount of black solid, the addition of hexane gave **3b**, which was collected by filtration and dried in vacuo (1.23 g, 2.35 mmol, 90%). $C_{19}H_{17}IN_2OPd$ (522.66): calcd. C 43.66, H 3.28, N 5.36, I 24.28; found C 43.54, H 3.53, N 5.35, I 24.38. ^1H NMR (300 MHz, $CDCl_3$, room temp.): δ = 2.32 (s, 6 H, Me), 7.08 (s, 1 H, *para*-C_6H_3), 7.26 (ddd, J = 9, 6, 1 Hz, 2 H, 5′-bpy), 7.40 (ddd, J = 8, 5, 1 Hz, 2 H, 5-bpy), 7.88 (s, 2 H, *ortho*-C_6H_3), 7.91 (dd, J = 5, 1 Hz, 1 H, 6′-bpy), 8.01 (ddd, J = 9, 6, 2 Hz, 1 H, 4- or 4′-bpy), 8.03 (ddd, J = 9, 8, 2 Hz, 1 H, 4- or 4′-bpy), 8.22 (d, J = 8 Hz, 1 H, 3- or 3′-bpy), 8.26 (d, J = 8 Hz, 1 H, 3- or 3′-bpy), 9.17 (d, J = 5 Hz, 1 H, 6-bpy) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, room temp.): δ = 21.1 (Me), 122.4 (3- or 3′-bpy), 123.1 (3- or 3′-bpy), 126.2 (5-bpy), 126.4 (5′-bpy), 128.4 (*ortho*-C_6H_3), 133.8 (*para*-C_6H_3), 137.5, 139.3 (2 C, 4- and 4′-bpy), 140.3, 150.0 (6′-bpy), 151.5 (6-bpy), 152.3, 154.6, 224.8 (C=O) ppm. The assignments of the NMR signals were supported by DEPT45, -90, and -135 as well as $^{13}C\{^1H\}$–^1H COSY spectra. IR (KBr disk, room temp.): $\tilde{\nu}$ = 1644 (C=O) cm^{-1}.

[PdI(COC_6H_4-2-OMe)(bpy)] (3e): Compound **3e** was prepared similarly to **3b**. The reaction of **1e** (69 mg, 0.14 mmol) and CO (1 atm) in CH_2Cl_2 (10 mL) at room temp. for 15 h yielded **3e** (48 mg, 0.091 mmol, 65%) as a yellow solid. $C_{18}H_{15}IN_2O_2Pd$ (524.63): calcd. C 41.21, H 2.88, N 5.34; found C 40.89, H 2.64, N 5.25. ^1H NMR ($CDCl_3$, 300 MHz, room temp.): δ = 3.84 (s, 3 H, OMe), 6.89 (d, J = 9 Hz, 1 H), 7.00 (dd, J = 7, 7 Hz, 1 H), 7.30–7.56 (3 H), 7.95–8.12 (4 H), 8.19 (d, J = 8 Hz, 1 H), 8.47 (d, J = 5 Hz, 1 H), 9.41 (d, J = 5 Hz, 1 H) ppm. $^{13}C\{^1H\}$ NMR spectroscopy. Low solubility prevented $^{13}C\{^1H\}$ NMR spectroscopy measurement. IR (KBr disk, room temp.): $\tilde{\nu}$ = 1667 (C=O) cm^{-1}.

[PdI{C(=N*t*Bu)Ph}(bpy)] (4a): To a CH_2Cl_2 (4.0 mL) solution of [PdI(Ph)(bpy)] (**1a**, 433 mg, 0.93 mmol) was added *t*BuNC (120 μL, 1.1 mmol). The reaction mixture was stirred for 12 h at room temp., the solution volume was increased by ca. 1 mL, and hexane (100 mL) was added. The separated solid was collected by filtration, washed with hexane, and dried in vacuo to yield **4a** as an orange powder (141 mg, 0.26 mmol, 28%). $C_{21}H_{22}IN_3Pd$ (549.73): calcd. C 45.88, H 4.03, N 7.64, I 23.08; found C 46.00, H 4.07, N 7.54, I 22.96. ^1H NMR (300 MHz, CD_2Cl_2, r. t.): δ = 1.65 (s, 9 H, Me), 7.22–7.25* (3 H, *meta*-Ph, *para*-Ph), 7.42 (ddd, J = 8, 5, 2 Hz, 1 H, 5′-bpy), 7.54 (ddd, J = 8, 6, 2 Hz, 1 H, 5-bpy), 7.98 (ddd, J = 7, 7, 2 Hz, 1 H, 4- or 4′-bpy), 8.01 (ddd, J = 8, 8, 2 Hz, 1 H, 4- or 4′-bpy), 8.07 (m, 1 H, 3- or 3′-bpy), 8.10 (m, 1 H, 3 or 3′-bpy), 8.18 (m, 2 H, *ortho*-Ph), 8.42 (ddd, J = 5, 2, 1 Hz, 1 H, 6′-bpy), 9.43 (ddd, J = 5, 2, 1 Hz, 1 H, 6-bpy) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, room temp.): δ = 32.5 (Me), 56.5 (*C*Me_3), 122.0, 122.8, 127.0, 127.1, 127.7, 128.3, 130.9, 139.0, 139.1, 143.2, 151.2, 152.3, 153.4, 155.6, 171.4 (C=N) ppm. IR (KBr disk, room temp.): $\tilde{\nu}$ = 1619 cm^{-1}.

[PdI{C(=N*t*Bu)C_6H_3-3,5-Me_2}(bpy)] (4b): Compound **4b** was prepared similarly to **4a**. The reaction of **1b** (989 mg, 2.0 mmol) and *t*BuNC (250 μL, 2.2 mmol) in CH_2Cl_2 (4.0 mL) at room temp. for 20 min yielded **4b** (1.09 g, 1.89 mmol, 94%) as an orange powder. $C_{23}H_{26}IN_3Pd$ (577.78): calcd. C 47.81, H 4.54, N 7.27; found C 47.54, H 4.69, N 7.21. ^1H NMR (300 MHz, $CDCl_3$, room temp.): δ = 1.67 [s, 9 H, $C(CH_3)_3$], 2.25 (s, 6 H, C_6H_3-3,5-*Me*$_2$), 6.83 (s, 1 H, *para*-C_6H_3), 7.24 (m, 2 H, *ortho*-C_6H_3), 7.30 (br, 1 H, 5′-bpy), 7.48 (br, 1 H, 5-bpy), 7.62 (d, J = 6 Hz, 1 H, 6′-bpy), 7.96–7.98 (2 H, 4- and 4′-bpy), 8.08 (2 H, 3- and 3′-bpy), 9.54 (6-bpy, J = 5 Hz, 1 H) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, room temp.): δ = 21.4 [$C(CH_3)_3$], 32.6 (C_6H_3-3,5-*Me*$_2$), 56.2 [*C*$(CH_3)_3$], 121.3, 122.1, 126.5, 126.6, 128.1, 129.8, 136.7, 138.3, 138.4, 142.5, 151.2, 152.4, 152.8, 155.0 ppm. IR (KBr disk, room temp.): $\tilde{\nu}$ = 1609 cm^{-1}.

[PdI{C(=NC_6H_3-2,6-Me_2)Ph}(bpy)] (5a): Compound **5a** was prepared similarly to **4a**. The reaction of **1a** (465 mg, 1.0 mmol) and (C_6H_3-2,6-Me_2)NC (130 mg, 0.10 mmol) in CH_2Cl_2 (45 mL) at room temp. for 14 h yielded **5a** (516 mg, 0.86 mmol, 86%) as a yellow solid. $C_{25}H_{22}IN_3Pd(H_2O)_{0.5}$ (606.8): calcd. C 49.48, H 3.82, N 6.92, I 20.91; found C 49.75, H 3.80, N 7.00, I 20.83. ^1H NMR (300 MHz, CD_2Cl_2, room temp.): δ = 2.10 (s, 6 H, Me), 6.84 (m, 1 H, *para*-C_6H_3), 6.92 (m, 2 H, *meta*-C_6H_3), 7.35–7.39* (4 H, *meta*-Ph, *para*-Ph, 5′-bpy), 7.49 (ddd, J = 8, 5, 1 Hz, 1 H, 5-bpy), 7.97 (ddd, J = 8, 8, 2 Hz, 2 H, 4-bpy), 7.99 (ddd, J = 8, 7, 1 Hz, 1 H, 4′-bpy), 8.05 (m, 1 H, 3- or 3′-bpy), 8.09 (m, 1 H, 3- or 3′-bpy), 8.29 (m, 1 H, 6′-bpy), 8.54 (m, 1 H, *ortho*-Ph), 9.37 (m, 1 H, 6-bpy) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, room temp.): δ = 20.6 (Me), 122.0, 122.5, 122.6, 126.9, 127.1, 128.0, 128.1, 129.6, 131.3, 139.1, 139.4, 141.8, 150.1, 151.4, 152.6, 153.5, 154.5, 155.8, 178.8 (C=N) ppm. IR (KBr disk, room temp.): $\tilde{\nu}$ = 1619 cm^{-1}.

Reactions of $AgBF_4$ with 1d, 1e, and 1g: A typical procedure for the reactions of $AgBF_4$ with [PdIAr(bpy)] [Ar = C_6H_4-4-OMe (**1d**), C_6H_4-2-OMe (**1e**), 1-naphthyl (**1g**)] is as follows. To an acetone (9.5 mL) solution of **1d** (102 mg, 0.205 mmol), $AgBF_4$ (78 mg,

0.40 mmol) in acetone (1.2 mL) was added with stirring at room temperature. The mixture was stirred for 1 h, and then excess NaCl (20 mg, 0.33 mmol) was added to the solution to quench the cationic or coordinatively unsaturated organopalladium complexes and stop the reaction. The resulting insoluble solid was removed by filtration, and the organic products were extracted with CH_2Cl_2. The products contained in the combined filtrate and extracts were analyzed by ^{1}H NMR spectroscopy. The yield of 4,4′-dimethoxybiphenyl (0.045 mmol, 43%) was estimated from the ^{1}H NMR peak area relative to those of dibenzyl added to the solution as an internal standard.

Reactions of $AgBF_4$, 1b and $[Pd(C_6H_4$-4-OMe)(acetone)$(PPh_3)_2]BF_4$ (6): The complex $[Pd(C_6H_4$-4-OMe)(acetone)$(PPh_3)_2]BF_4$ (**6**) was generated in situ by the reaction of $AgBF_4$ (77 mg, 0.40 mmol) and $[PdI(C_6H_4$-4-OMe)$(PPh_3)_2]$ (87 mg, 0.10 mmol) in acetone (1.0 mL). To the above solution **1b** (50 mg, 0.10 mmol) in acetone/CH_2Cl_2 (10/10 mL) was added dropwise over 30 min. The mixture was stirred for 1 h at room temperature, the resulting insoluble solid was removed by filtration, and the organic products were extracted with Et_2O. The products in the combined filtrate and extracts were analyzed by ^{1}H NMR spectroscopy and GC–MS. The yields of 3,3′,5,5′-tetramethylbiphenyl (0.020 mmol, 20%), 4,4′-dimethoxybiphenyl (0.0089 mmol, 9%), and $MeOC_6H_4$-4-(C_6H_3–3,5-Me_2) (0.051 mmol, 51%) were estimated from the ^{1}H NMR peak areas relative to those of 1,1,2,2-tetrachloroethane added to the solution as an internal standard.

Reactions of $AgBF_4$ with 1b and 1c: To an acetone (10 mL) solution of **1b** (51 mg, 0.10 mmol), **1c** (61 mg, 0.10 mmol) and $AgBF_4$ (86 mg, 0.44 mmol) were added with stirring at room temperature. The mixture was stirred for 1 h, and excess NaI (94 mg, 0.63 mmol) was added to the solution to quench the cationic or coordinatively unsaturated organopalladium complexes and stop the reaction. The resulting insoluble solid was removed by filtration, and the organic products were extracted with Et_2O. The products contained in the combined filtrate and extracts were analyzed by GC–MS and ^{1}H NMR spectroscopy. The yield of 4,4′-dimethoxybiphenyl (0.045 mmol, 43%) was estimated from the ^{1}H NMR peak area relative to those of 1,3,5-trimethylbenzene added to the solution as an internal standard.

Reactions of $AgBF_4$ with 3b and 3e: A typical procedure for the reactions of $AgBF_4$ with [PdI(COAr)(bpy)] [Ar = C_6H_3-3,5-Me_2 (**3b**), C_6H_4-2-OMe (**3e**)] is as follows. To an acetone (10 mL) solution of **3b** (65 mg, 0.12 mmol), $AgBF_4$ (32 mg, 0.17 mmol) was added with stirring at room temperature. The mixture was stirred for 1 h, and excess NaI (57 mg, 0.38 mmol) was added to the solution to quench the cationic or coordinatively unsaturated organopalladium complexes and stop the reaction. The resulting insoluble solid was removed by filtration, and the organic products were extracted with acetone, hexane, and Et_2O. The products contained in the combined filtrate and extracts were analyzed by ^{1}H NMR spectroscopy and GC–MS. The yield of 3,3′,5,5′-tetramethylbenzophenone (0.045 mmol, 51%) was estimated from the ^{1}H NMR peak area relative to those of mesitylene added to the solution as an internal standard.

Reactions of $AgBF_4$ with 3b Under CO: To an acetone (10 mL) solution of **3b** (479 mg, 0.92 mmol), $AgBF_4$ in acetone was added with stirring at room temperature under CO. The resulting insoluble solid was removed by filtration, and hexane (50 mL) was added to induce the separation of an off-white solid from the solution. The solid was collected by filtration, washed with hexane, and dried in vacuo to yield $[Pd(CO)(COC_6H_3$-3,5-$Me_2)$(bpy)]BF_4 (**7**-CO; 155 mg, 35%). ^{1}H NMR (400 MHz, [D_6]acetone, room temp.): δ = 2.40 (s, 6 H, Me), 7.45 (s, 1 H, *para*-C_6H_3), 7.87 (dd, J = 6 Hz, 2 H, 5-bpy), 8.04 (s, 2 H, *ortho*-C_6H_3), 8.45 (ddd, J = 7, 7, 2 Hz, 2 H, 4-bpy), 8.58 (br. s, 2 H, 6-bpy), 8.75 (d, J = 8 Hz, 2 H, 3-bpy) ppm. ^{1}H NMR (400 MHz, [D_6]acetone, –30 °C): δ = 2.54 (s, 6 H, Me), 7.45 (s, 1 H, *para*-C_6H_3), 7.84 (br. s, 1 H, 5- or 5′-bpy), 7.95 (br. s, 1 H, 5- or 5′-bpy), 8.04 (s, 2 H, *ortho*-C_6H_3), 8.19 (br. s, 1 H, 3- or 3′-bpy), 8.46 (ddd, J = 8, 8, 2 Hz, 2 H, 4- and 4′-bpy), 8.77 (br. s, 2 H, 3- and 3′-bpy), 8.96 (br. s, 1 H, 3- or 3′-bpy) ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_3NO_2, room temp.): δ = 15.7 (Me), 119.4 (3- and 3′-bpy), 123.6 (5- and 5′-bpy), 124.7 (C_6H_3-*ortho*), 132.6 (C_6H_3-*para*), 133.0, 135.5, 137.8, 147.3 (4- and 4′-bpy), 151.4 (2- and 2′-bpy), 168.4 (C≡O), 208.5 (C=O) ppm. The signals of 6- and 6′-bpy were not detected. IR (KBr disk, room temp.): $\tilde{\nu}$ = 2149 (C≡O) cm^{-1}.

Reactions of H_2O with [PdI{C(=N*t*Bu)C_6H_3-3,5-Me_2}(bpy)] (4b): To a toluene (2.0 mL) suspension of **4b** (58.0 mg, 0.10 mmol), H_2O (100 μL, 5.6 μmol) was added with stirring at room temperature. The mixture was stirred for 120 h at 50 °C, the resulting insoluble solid was removed by filtration, and evaporation of the filtrate yielded a mixture containing *t*BuNHCO(C_6H_3-3,5-Me_2) (0.042 mmol, 42%) and bpy (0.021 mmol, 21%). The products contained in the combined filtrate and extracts were analyzed by ^{1}H NMR spectroscopy and GC–MS. The yields of *t*BuNHCO(C_6H_3-3,5-Me_2) and bpy were estimated from their ^{1}H NMR peak areas relative to those of 1,1,1,2-tetrachroloethane added to the solution as an internal standard. *t*BuNHCO(C_6H_3-3,5-Me_2): GC–MS: m/z = 205. ^{1}H NMR (300 MHz, $CDCl_3$, room temp.): δ = 1.44 [s, 9 H, $C(CH_3)_3$], 2.32 (s, 6 H, C_6H_3-3,5-*Me*$_2$), 5.91 (br, 1 H, NH), 7.08 (dd, J = 1, 1 Hz, 1 H, *para*-C_6H_3), 7.29 (d, J = 1 Hz, 2 H, *meta*-C_6H_3) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, room temp.): δ = 21.2 [$C(CH_3)_3$], 28.8 (C_6H_3-3,5-*Me*$_2$), 51.5 [*C*$(CH_3)_3$], 124.5, 132.6, 135.9, 138.1, 167.3 (C=O) ppm. IR (KBr disk, room temp.): $\tilde{\nu}$ = 3305 (N–H), 1638 (C=O) cm^{-1}.

Reactions of $AgBF_4$ with 1h: To a CH_2Cl_2 (1.0 mL) solution of **1h** (99 mg, 0.081 mmol), $AgBF_4$ (48 mg, 0.24 mmol) in acetone (0.7 mL) was added with stirring at room temperature. The formation of Pd metal as a black solid was observed. The mixture was stirred for 1 h, and excess NaCl (17 mg) was added to the solution to stop the reaction. The resulting insoluble solid was removed by filtration, and the organic products were extracted with CH_2Cl_2. The products in the combined filtrate and extracts were analyzed by ^{1}H NMR spectroscopy and ESI-MS. The yield of **1d** (0.031 mmol, 38%) was estimated from the ^{1}H NMR peak area relative to those of dibenzyl added to the solution as an internal standard.

X-ray Structure Analyses: Single crystals of **1d**, **1e**, **1f**, **3b**, **4a**, and **5a** were obtained by recrystallization from CH_2Cl_2/Et_2O, CH_2Cl_2/Et_2O, CH_2Cl_2/Et_2O, $CHCl_3$/hexane, CH_2Cl_2/MeOH, and CH_2Cl_2/Et_2O, respectively.

CCDC-1017091 (for **1d**), -1017092 (for **1e**$_3$·CH_2Cl_2), -1017093 (for **1f**·CH_2Cl_2), -1017094 (for **3b**·$CHCl_3$), -1017095 (for **4a**), and -1017096 (for **5a**) 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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