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Synthesis and Structure of Dinuclear Silver(I) and Palladium(II) Complexes of 2,7-Bis(methylene)naphthalene-Bridged Bis-N-Heterocyclic Carbene Ligands

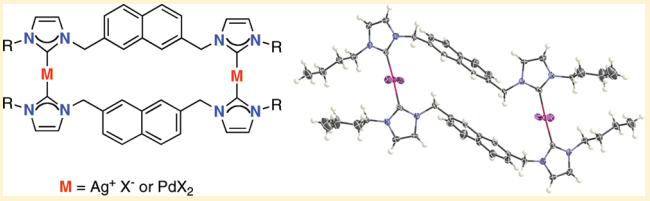
Shinichi Saito,*[,†] Mitsuya Saika,[†] Ryu Yamasaki,[†] Isao Azumaya,[‡] and Hyuma Masu[‡]

[†]Department of Chemistry, Faculty of Science, Tokyo University of Science, Kagurazaka, Shinjuku, Tokyo 162-8601, Japan

[‡]Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, Shido, Sanuki-city, Kagawa 769-2193, Japan

Supporting Information

ABSTRACT: We synthesized a series of new Ag_2(bis-NHC)$_2$ complexes from the corresponding bisimidazolium salts tethered with 2,7-dimethylnaphthalene-bridged bis-NHC ligands. The reaction proceeded in a selective manner, and the Ag_2(bis-NHC)$_2$ complexes were isolated in good to high yields. The Ag complexes were converted to the Pd_2(bis-NHC)$_2$ complexes efficiently. It is important to choose proper conditions for the conversion of the silver complexes to the palladium complexes, depending on the structure of the ligand: the effect of the counteranion was significant. The structures of the complexes were studied by X-ray crystallographic analyses and compared with the corresponding monodentate NHC complexes. The catalytic activity of the Pd complexes for the Mizoroki−Heck reaction was examined.



The chemistry of transition-metal complexes containing N-heterocyclic carbenes (NHCs) has been extensively studied, and a large number of compounds have been reported. Among various metal complexes, the Ag-NHC complexes turned out to be very unique, since they are fluxional molecules and also efficient carbene-transferring reagents. The structures of these complexes were also interesting, and many examples have been reported in the literature.[1] The compounds could be readily prepared by the reaction of the imidazolium salt with Ag_2O, and it is not necessary to isolate NHC, which is a less stable species. Interestingly, few 1:1 complexes were reported,[2] while a series of 2:1 (Ag_2(bis-NHC)) complexes[3,4] and 2:2 (Ag_2(bis-NHC)$_2$) complexes[5−7] were characterized. Even cyclic bisimidazolium salts reacted with Ag_2O to give interesting 2:2 complexes.[8] Many of these Ag-NHC complexes were known as good carbene-transfer agents, and various metal-NHC complexes have been synthesized. Among the complexes, the Pd-NHC complexes[9] have been extensively studied since the complexes are potentially useful catalysts for organic synthesis. In contrast to the corresponding Ag-NHC complexes, a limited number of dinuclear Pd complexes have been reported in the literature.[10]

We have been interested in the chemistry of metal-bis-NHC and metal-NHC-oxazoline complexes and synthesized some Pd complexes with unique structures.[11] In this paper we report the synthesis and structure of new dinuclear silver and palladium complexes that are connected with 2,7-dimethylnaphthalene-bridged bis-NHC ligands.[11] The catalytic activities of the Pd complexes were also examined.

RESULTS AND DISCUSSION

Synthesis and Structure of the Silver Complexes. The syntheses of dinuclear Ag complexes are summarized in Schemes 1 and 2. Thus, the reaction of bis(2,7-bromomethyl)naphthalene (**1**)[13] with substituted imidazoles (**2a**−**c**) proceeded smoothly to give the corresponding bisimidazolium bromides (**3a**−**c**) in good yields. It was important to carry out the reaction in acetonitrile for the synthesis of **3a** and **3c**: the solubility of the substituted imidazoles in organic solvents was low, and the formation of monoimidazolium salt was observed. On the other hand, the solubility of **2b** was sufficiently high, and the reaction proceeded smoothly in acetone or other common organic solvents. The bromides (**3a** and **3c**) were converted to the corresponding hexafluorophosphates. The reactions of bisimidazolium bromides (**3a** and **3b**) with Ag_2O in the presence of molecular sieves in CH_2Cl_2[14] gave **5a** and **5b** in moderate yields (Scheme 2). Though the formation of various isomeric compounds such as 1:1 complex, 2:1 (Ag_2(bis-NHC)) complex, 2:2 (Ag_2(bis-NHC)$_2$) complex, and other oligomeric (polymeric) complexes is possible, only the 2:2 complexes were isolated. The bisimidazolium hexafluorophosphates **4a** and **4c** were treated with Ag_2O in the presence of a phase-transfer catalyst[15] to give similar 2:2 complexes (**6a** and **6c**). Compound **6a** was also synthesized by the reaction of **5a** in the presence of an excess (20 equiv) of KPF_6 in CH_2Cl_2.

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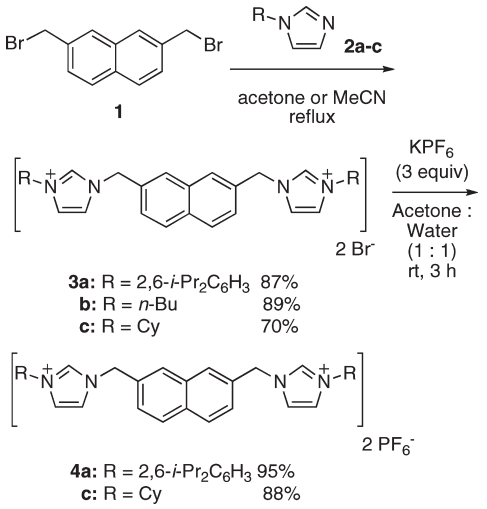
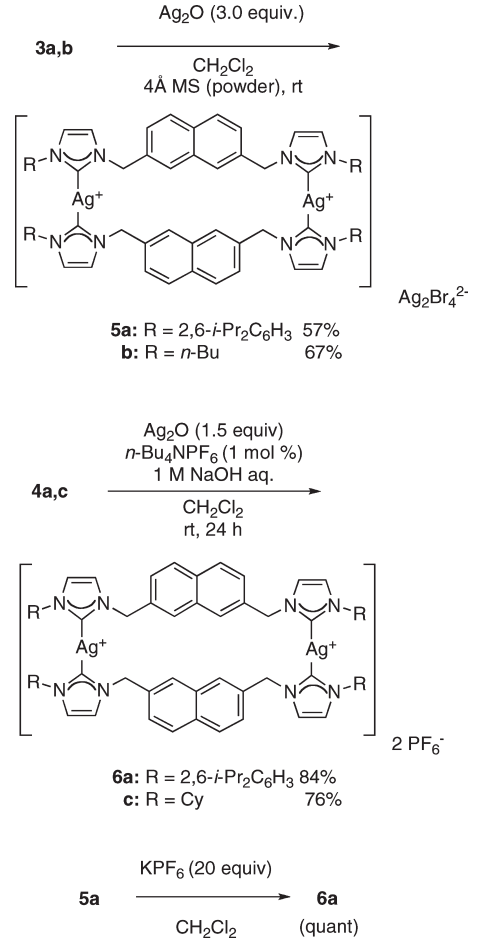
Scheme 1. Synthesis of Bisimidazolium Salts



Scheme 2. Synthesis of Dinuclear Silver-Carbene Complexes



The structures of the complexes were studied by ^{1}H NMR spectroscopy, and the observed spectra were in accordance with the expected structures of the complexes. For example, the resonance of the methyl group of **4a** appeared as two pairs of doublets at 1.11 and 1.09 ppm. The resonance of the methyl group of the corresponding Ag complex (**6a**) shifted significantly, and the doublets appeared at 1.06 and 0.85 ppm. The observed high-field shift of the resonance of the methyl group could be explained in terms of the effect of the other aromatic ring located close to the methyl group in **6a**.

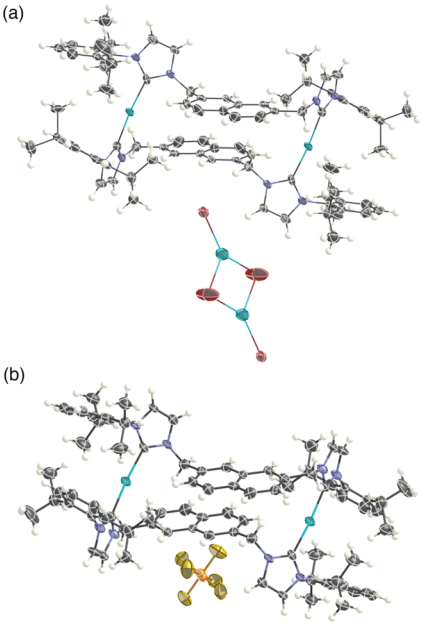


Figure 1. Crystal structure of **5a** (a) and **6a** (b) drawn as thermal ellipsoid models. Solvent molecules are omitted for clarity.

Table 1. Selected Bond Lengths and Angles for the Silver Complexes

compound	Ag−C (Å)	C−Ag−C (deg)	dihedral angle[a] (deg)
5a	2.09(1)	173.5(4)	63
	2.09(1)		
6a	2.072(8)	174.9(3)	49
	2.102(8)		
$[Ag(IPr)_2]PF_6$[b]	2.077(4)	173.9(2)	70
	2.074(4)		

[a] The angle between the planes of the two imidazolin-2-ylidene rings. See ref 18. [b] Data collected from ref 17.

Recrystallization of **5a** from acetone/hexane gave a single crystal, and the X-ray structure is shown in Figure 1a. This complex consists of a dinuclear $Ag_2(bis\text{-}NHC)_2^{2+}$ cation and a rather uncommon $Ag_2Br_4^{2-}$ anion,[16] and it exists as a *trans* isomer. The molecular structure of **6a** was also analyzed, and the crystal structure is shown in Figure 1b. The selected bond distances and angles of **5a** and **6a** are compared with structurally similar complexes, and the results are summarized in Table 1. The bond angles and the bond distances between the Ag atom and the adjacent C atoms in **5a** and **6a** are similar to those of a mononuclear Ag complex, $[Ag(IPr)_2]PF_6$.[17] On the other hand, the dihedral angles[18] between the plains of the two imidazolin-2-ylidene rings (63° for **5a** and 49° for **6a**) are smaller compared to the dihedral angle in $[Ag(IPr)_2]PF_6$. The observed smaller angles could be explained in terms of the presence of a less bulky substituent (naphthylmethyl group, instead of the diisopropylphenyl group) bound to the imidazolin-2-ylidene ring.

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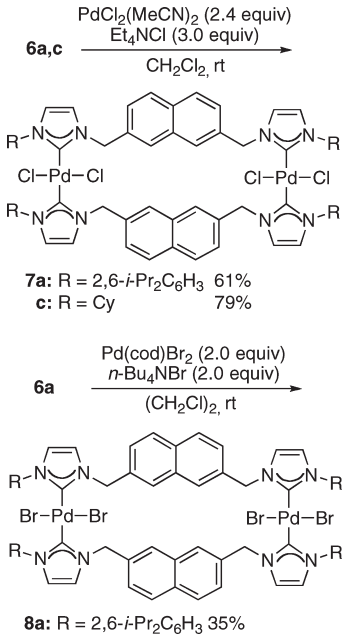
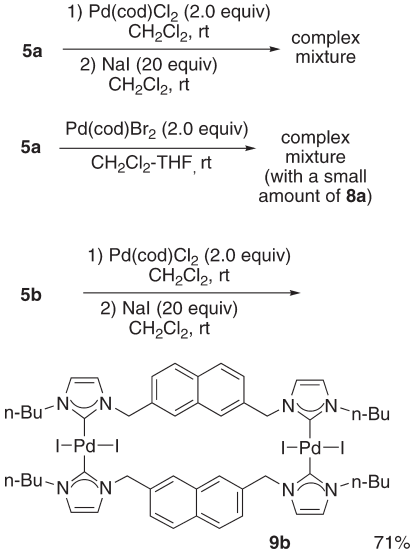
Scheme 3. Synthesis of Dinuclear Palladium-Carbene Complexes from 6



Scheme 4. Synthesis of Dinuclear Palladium-Carbene Complexes from 5



The syntheses of dinuclear palladium complexes were achieved by the metal exchange reaction of the corresponding silver complexes. For example, the $PdCl_2$ complex **7a** was prepared by the reaction of **6a** with $Pd(MeCN)_2Cl_2$ in the presence of tetraethylammonium chloride in 61% yield (Scheme 3). The addition of tetraethylammonium chloride is essential for the isolation of **7a** in pure form. We assume that the supply of the halogen anion from the ammonium salt is important for the efficient synthesis of **7a**. Compound **6c** reacted in a similar manner, and the palladium complex **7c** was synthesized. We also succeeded in the synthesis of the $PdBr_2$ complex

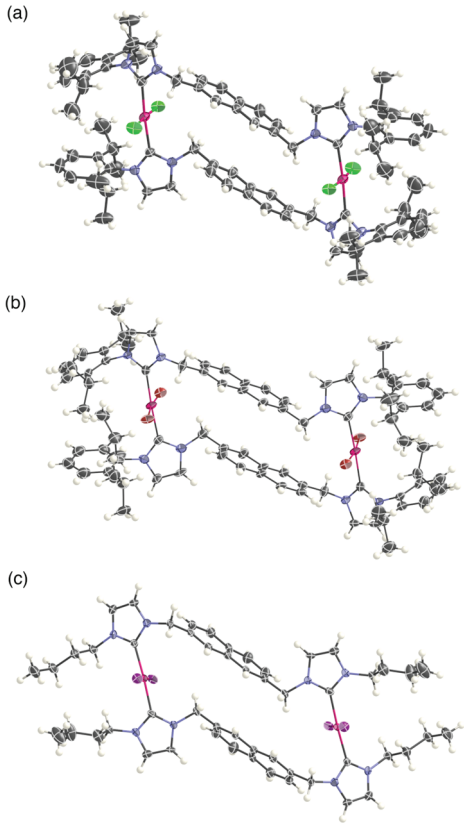


Figure 2. Crystal structure of Pd complexes **7a** (a), **8a** (b), and **9b** (c) drawn with thermal ellipsoid models. Solvent molecules are omitted for clarity.

(**8a**) by carrying out the reaction of **6a** with $Pd(cod)Br_2$-*n*-Bu_4NBr. On the other hand, the synthesis of the palladium complexes from **5a** turned out to be less successful (Scheme 4). Thus, the treatment of **5a** with $Pd(cod)Cl_2$ and NaI[19] resulted in the formation of a complex mixture. We speculated that the halogen exchange reaction might cause the decomposition and used $Pd(cod)Br_2$ for the reaction so that the halogen exchange reaction is unnecessary, but the formation of a complex mixture was observed, together with a small amount of **8a**. The synthesis of the corresponding palladium complex from **5b** was successful, and compound **9b** was isolated in 71% yield. The successful synthesis of **9b** and the formation of a complex mixture in the reaction of **5a** with palladium complexes could be explained in terms of the bulkiness of the ligands. In the presence of a bulky substituent, the formation of the 2:2 (Pd_2(bis-NHC)$_2$) complex would be prevented due to the steric hindrance, and the oligomerization reaction will proceed preferentially.

The molecular structures of **7a**, **8a**, and **9b** were analyzed by X-ray diffraction, and the crystal structures are shown in Figure 2. The selected bond distances and angles of the palladium complexes and a structurally similar palladium complex, $[Pd(IPr)_2]Cl_2$[20] (**14**), are summarized in Table 2.

The lengths of the Pd−C bonds were similar to those of **14**, and the effects of the structure of the complexes on the lengths of the Pd−C bonds were not significant. The C−Pd−C angles were 175−180°, and all of the complexes analyzed in this study exist as *trans* isomers. On the other hand, the dihedral angle between the two NHC moieties of the Pd complexes were different from each other. For example, the dihedral angle of

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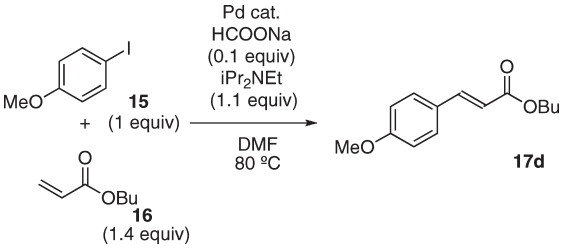
Table 2. Selected Bond Lengths and Angles for the Palladium Complexes

compound	Pd−C (A)	C−Pd−C (deg)	dihedral angle[a] (deg)	Pd−halogen (Å)
7a	2.027(3)	175.7(1)	32	2.316(1)
	2.030(3)			
8a[b]	1.997(8)	177.3(3)	36	2.439(1)
	2.016(8)			2.443(1)
	2.031(7)	176.9(3)	32	2.438(6)
	2.045(7)			2.6112(6)
9b	2.02(1)	176.0(4)	24	2.6058(6)
	2.03(1)			2.6112(6)
$[Pd(IPr)_2]Cl_2$[c] (**14**)	2.054(4)	179.0(2)	40	2.299(2)
	2.019(6)			2.303(2)

[a] Ref 18. [b] Two molecules of **8a** are included in the asymmetric unit of the crystal. [c] Data collected from ref 20.

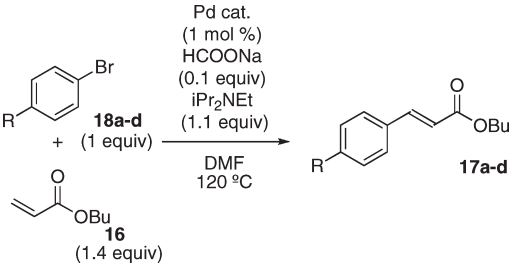
Table 3. Catalytic Activity of the Pd Complexes for the Mizoroki−Heck Reaction between 4-Iodoanisole (15) and Butyl Acrylate (16)



entry	Pd cat.	amount (mol %)	time (h)	yield of **17d** (%)
1	**9b**	1	2	94
2		0.01	23	88
3[a]		1	6	92
4	**7a**	1	1	93
5	**7c**	1	1	93

[a] The reagent-grade DMF was used as the solvent, and the reaction was carried under air.

Table 4. Catalytic Activity of the Pd Complexes for the Mizoroki−Heck Reaction between Aryl Bromides (18a−d) and 16



entry	Pd cat.	cmpd	R	time (h)	yield of **17** (%)
1	**9b**	**18a**	NO_2	17	88
2		**18b**	$COCH_3$	14	92
3		**18c**	H	24	5
4		**18d**	OMe	24	18
5	**7a**	**18a**	NO_2	19	79
6		**18b**	$COCH_3$	19	78
7		**18d**	OMe	24	trace
8	**7c**	**18a**	NO_2	6	94
9		**18b**	$COCH_3$	5	75
10		**18c**	H	24	15

7a was smaller than that of **14**. The observed smaller angles of **7a** as well as **8a** could be explained in terms of the presence of a smaller substituent (naphthylmethyl group) or the dimeric structure of the complex. The dihedral angle of **9b** was even smaller compared to that of **14**. We assume that the presence of a less bulky substituent (butyl group) instead of the bulkier IPr group induced the reduction of the dihedral angle.

Finally, the catalytic activity of the Pd complexes in the Mizoroki−Heck reaction was examined. We employed the reaction conditions reported by Roland, Jutand, and co-workers.[21] Thus, the aryl halide and butyl acrylate (**16**) were reacted in the presence of the Pd complex, sodium formate, and diisopropylethylamine in DMF. The results are summarized in Tables 3 and 4.

4-Methoxy-1-iodobenzene (**15**) reacted with **16** in the presence of **9b** (1 mol %) at 80 °C for 2 h, and the coupling product (**17d**) was isolated in 94% yield (Table 3, entry 1). The reaction proceeded even when the amount of **9b** was reduced to 0.01 mol %, and compound **17d** was isolated in 88% yield after heating the reaction mixture for 23 h (entry 2). In this reaction, the turnover number (TON) reached 8800, which is comparable to the TON (14 600, 73% conversion in the reaction of iodobenzene with butyl acrylate) reported by Roland, Jutand, and co-workers.[21] The product was isolated in 92% yield when the reaction was carried under air and reagent-grade DMF was used; however, the catalytic activity of **9b** decreased and a longer reaction time was required (entry 3). Other Pd complexes such as **7a** and **7c** were efficient catalysts for this reaction (entries 4 and 5).

We also examined the Mizoroki−Heck reaction of aryl bromides (Table 4). The reactions of electron-deficient aryl bromides such as 1-bromo-4-nitrobenzene (**18a**) or 4-nitrobenzophenone (**18b**) with **16** proceeded smoothly in the presence of 1 mol % of **9b** at 120 °C, and the products were isolated in high yields (entries 1 and 2). Bromobenzene (**18c**) and 4-bromoanisole (**18d**) turned out to be inferior substrates for this reaction, and the yields of the product were very low even when the reaction mixture was heated for 24 h (entries 3 and 4). The catalytic activity of **7a** was lower compared to that of **9b**, and the

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yields of the coupling products slightly decreased (entries 5 and 6). The reactivity of 4-bromoanisole (**18d**) turned out to be very low when the reaction was carried out in the presence of **7a**, and only a trace amount of the product was isolated (entry 7). Meanwhile, the catalytic activity of **7c** was much higher compared to other complexes: the reaction of **18a** completed in 6 h and the product was isolated in 94% yield (entry 8). The reaction of **18b** also proceeded smoothly (entry 9). The reaction of **18c** was, however, sluggish, and the yield of **17d** was low (entry 10). In our study, the Pd complex with the ICy-type ligand (*N*-cyclohexylimidazolidene ligand, i.e., **7c**) turned out to be a better catalyst compared to the Pd complex with the IPr ligand or the *N*-butylimidazolidene ligand (**9b** or **7a**). The result is in contrast to the generally observed high reactivity of the Pd-IPr complex for various reactions.[9c] The reason for the high catalytic activity of **7c** is not clear at present.

CONCLUSION

We synthesized a series of new Ag_2(bis-NHC)$_2$ complexes from the corresponding bisimidazolium salts tethered with a rigid linker that contains the naphthalene moiety. The reaction proceeded in a selective manner, and the Ag_2(bis-NHC)$_2$ complexes were isolated in good to high yields. The Ag complexes were converted to the Pd_2(bis-NHC)$_2$ complexes efficiently. The structures of the complexes were elucidated and compared with the corresponding monodentate NHC complexes. The catalytic activity of the Pd complexes for the Mizoroki−Heck reaction was examined. The study revealed that the bisimidazolium salts connected with the rigid 2,7-bis(methylene)naphthalene moiety are useful precursors for the synthesis of (metal)$_2$(bis-NHC)$_2$ complexes.

EXPERIMENTAL SECTION

General Procedure for the Synthesis of the Bis-imidazolium Bromide Salts (Scheme 1, 3a−c). To a stirred solution of 2,7-bis(bromomethyl)naphthalene (**1**) (1.0 mmol) in solvent (acetone (4 mL, for **3b**) or acetonitrile (12 mL, for **3a** and **3c**)) was added 1-substituted-imidazole (**2a**−**c**) (2.1 mmol). After the mixture was refluxed for 3−16 h, the resulting precipitate was separated and washed by Et_2O. The collected solid was purified by recrystallization or silica gel column chromatography (MeOH/CH_2Cl_2, 10:1).

*[2,7-Bis(2-N-(2,6-diisopropylphenyl)imidazolinium)methyl] Bromide, [Napht-Ipr$_2$]-Br$_2$ (**3a**).* The crude product was purified by recrystallization (CH_2Cl_2/Et_2O) to give a colorless solid: mp 194.0−197.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.49 (s, 2H) 8.28 (s, 2H), 8.14 (s, 2H) 7.65 (d, J = 8.4 Hz, 2H), 7.50−7.43 (m, 4H), 7.26−7.23 (m, 4H), 7.11 (s, 2H), 6.23 (s, 4H), 2.20 (quint, J = 6.9 Hz, 4H), 1.18 (d, J = 6.6 Hz, 12 H), 1.08 (d, J = 6.6 Hz, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.3, 137.5, 132.8, 132.6, 131.9, 131.7, 130.2, 129.6, 128.7, 126.3, 124.6, 124.2, 124.1, 52.7, 28.6, 24.5, 23.9; IR (KBr) 3465, 2958, 2742, 2471, 2374, 2074, 1717, 1640, 1560, 1540, 1513, 1458, 1415, 1387, 1367, 1336, 1309, 1278, 1256, 1242, 1188, 1147, 1116, 1070, 1042, 1022, 957, 936, 857, 807, 760, 673, 631, 576, 558, 526, 499, 470; HRMS-ESI (m/z) [M − Br]$^+$ calcd for $C_{42}H_{50}BrN_4$, 689.3213; found, 689.3232.

*[2,7-Bis(2-N-n-butyl)imidazolinium]methyl] Bromide, [Napht-n-Bu$_2$]-Br$_2$ (**3b**).* The crude product was dissolved in CH_2Cl_2 (1 mL), and Et_2O (16 mL) was added to the solution to give a brown, gummy solid, which was washed by Et_2O and dried to give a very hygroscopic yellow, amorphous solid: ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.42 (s, 2H), 8.00 (d, J = 9.0 Hz, 2H), 7.97 (s, 2H), 7.85 (d, J = 13.2 Hz, 4H), 7.58 (d, J = 8.4 Hz, 2H), 5.62 (s, 4H), 4.18 (t, J = 7.2 Hz, 4H), 1.77 (quint, J = 7.2 Hz, 4H), 1.25 (sext, J = 7.2 Hz, 4H), 0.88 (t, J = 7.2 Hz, 6H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 136.5, 133.3, 132.7, 129.0, 127.9, 126.7, 123.1, 122.9, 52.2, 49.0, 31.5, 19.0, 13.5 (2-imidazolium-CH was not observed); IR (KBr) 3422, 3128, 3062, 2959, 2872, 2407, 2056, 1742, 1610, 1560, 1515, 1459, 1358, 1156, 1022, 948, 920, 855, 743, 630, 554, 475; HRMS-ESI (m/z) [M − Br]$^+$ calcd for $C_{26}H_{34}BrN_4$, 481.1961; found, 481.1985.

*[2,7-Bis(2-N-cyclohexyl)imidazolinium]methyl] Bromide, [Napht-Cy$_2$]-Br$_2$ (**3c**).* The crude product was purified by silica gel chromatography to give a very hygroscopic yellow, amorphous solid: ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.62 (s, 2H), 8.01 (s, 2H) 8.00 (d, J = 8.4 Hz, 2H), 7.97 (s, 2H), 7.92 (s, 2H), 7.63 (dd, J = 9.0, 1.2 Hz, 2H), 5.64 (s, 4H), 4.32 (tt, J = 12.0, 3.6 Hz, 2H), 2.07 (d, J = 10.8 Hz, 4H), 1.81 (d, J = 13.8 Hz, 4H), 1.71−1.63 (m, 6H), 1.37 (qt, J = 12.6, 3.6 Hz, 4H), 1.20 (qt, J = 13.2, 3.6 Hz, 2H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 135.3, 133.3, 132.6, 128.9, 128.0, 126.8, 122.7, 121.4, 58.9, 52.7, 32.6, 24.6, 24.5 (2-imidazolium-CH was not observed); IR (KBr) 3418, 3127, 3063, 2933, 2856, 2365, 2053, 1634, 1556, 1510, 1449, 1363, 1269, 1241, 1154, 1028, 989, 924, 897, 854, 750, 650, 628, 471, 441, 411; HRMS-ESI (m/z) [M − Br]$^+$ calcd for $C_{30}H_{38}BrN_4$, 533.2274; found, 533.2269.

General Procedure for the Synthesis of the Bis-imidazolium Hexafluorophosphates (Scheme 1, 4a and 4c). The imidazolium salt **3** (1 mmol) was dissolved in a mixture of water (5 mL) and acetone (5 mL), and then potassium hexafluorophosphate (0.55 g, 3 mmol) was added. The reaction mixture was stirred at rt for 3 h and monitored by TLC. The acetone was evaporated under reduced pressure, and the water layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was washed three times with water (3 × 10 mL) and dried over Na_2SO_4. The solvent was removed in vacuo to give hexafluorophosphate salt **4**.

*[2,7-Bis(2-N-(2,6-diisopropylphenyl)imidazolinium)methyl] Hexafluorophosphate, [Napht-Ipr$_2$]-2PF$_6$ (**4a**):* colorless solid; mp 289.0−289.9 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.75 (s, 2H), 8.15 (dt, J = 13.2, 1.2 Hz 4H), 8.07 (d, J = 8.4 Hz, 2H), 7.97 (s, 2H), 7.62 (t, J = 7.8 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 7.8 Hz, 4H), 5.74 (s, 4H), 2.23 (sept, J = 6.0 Hz, 4H), 1.11 (dd, J = 10.8, 6.6 Hz, 24H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 145.2, 138.3, 133.3, 132.7, 131.7, 130.7, 129.2, 127.8, 126.3, 125.7, 124.6, 124.6, 123.8, 52.9 28.3, 24.0, 23.8; IR (KBr) 3154, 3094, 3080, 2968, 2931, 2874, 2360, 2342, 1616, 1548, 1458, 1416, 1368, 1184, 1107, 1071, 840, 740, 671, 627, 558, 457. Anal. Calcd for $C_{42}H_{50}F_{12}N_4P_2$: C, 56.00; H, 5.59; N, 6.22. Found: C, 55.70; H, 5.37; N, 6.14.

*[2,7-Bis(2-N-cyclohexyl)imidazolinium]methyl] Hexafluorophosphate, [Napht-Cy$_2$]-2PF$_6$ (**4c**):* colorless solid; mp 206.0 °C−209.2 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ 9.37 (s, 2H), 8.00 (d, J = 8.4 Hz, 2H) 7.93 (d, J = 12.6 Hz 4H), 7.83 (s, 2H), 7.58 (d, J = 9.0 Hz, 2H), 5.57 (s, 4H), 4.29 (tt, J = 12.0, 3.6 Hz, 2H), 2.07 (d, J = 12.6 Hz, 4H), 1.83 (d, J = 13.2 Hz, 4H), 1.70−1.65 (m, 6H), 1.37 (qt, J = 13.2, 3.6, 4H), 1.19 (qt, J = 13.2, 3.6, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 135.3, 133.2, 132.7, 129.0, 127.9, 126.8, 122.8, 121.5, 59.0, 52.3, 32.6, 24.7, 24.6 (2-imidazolium-CH was not observed); IR (KBr) 3674, 3396, 3168, 3108, 2930, 2860, 2671, 1557, 1454, 1348, 1270, 1177, 1154, 1109, 1025, 992, 843, 779, 738, 704, 650, 629, 558, 479, 419. Anal. Calcd for $C_{30}H_{38}F_{12}N_4P_2$: C, 48.39; H, 5.14; N, 7.52. Found: C, 48.60; H, 5.13; N, 7.40.

Synthesis of Dinuclear Silver-Carbene Complexes (Scheme 2). *General Procedure for Synthesis of Dinuclear Silver-Carbene Complex Ag$_2$Br$_3$ Salts (**5a**,**b**).* A mixture of CH_2Cl_2 (40 mL), imidazolium salt (Br^-) **3** (1 mmol), 4 Å molecular sieves (2 g), and silver(I) oxide (1.5 mmol) was stirred vigorously in the dark at rt for 24 h. The reaction was monitored by ^{1}H NMR. After filteration through Celite, the filtrate was evaporated to give the crude product. The crude product was purified by recrystallization (CH_2Cl_2/Et_2O) to afford Ag($Ag_2Br_4^{2-}$) complexes **5**.

*[Napht-Ipr$_2$]$_2$Ag$_2$-Ag$_2$Br$_4$ (**5a**):* colorless solid; yield 57% (0.440 g); mp 241.5−242.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90−7.84 (m, 8H), 7.48−7.39 (m, 8H), 7.25−7.20 (m, 12H), 7.01 (s, 4H), 5.58 (s, 8H), 2.39 (quant, J = 5.7 Hz, 8H), 1.24 (d, J = 6.6 Hz, 24H), 1.11 (d, J = 6.9 Hz, 24H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.6, 134.6, 133.8, 130.6, 129.3, 127.7, 125.7, 124.3, 121.1, 56.0, 28.4, 24.7, 24.3 (carbene-C and four aromatic C were not observed: at higher concentration, the broadening of the signals was observed); IR (KBr) 3482, 3155, 3124, 3077, 2965, 2922, 2869, 2597, 2360, 1536, 1514, 1472, 1416, 1385, 1362, 1317, 1249, 1225, 1181, 1105, 1058, 1032, 959, 939, 902, 839, 806, 757, 628, 470, 433, 419. Anal. Calcd for $C_{84}H_{96}Ag_4Br_4N_8$: C, 51.24; H, 4.91; N, 5.69. Found: C, 51.18; H, 4.89; N, 5.54.

*[Napht-n-Bu$_2$]$_2$Ag$_2$-Ag$_2$Br$_4$ (**5b**):* colorless solid; yield 67% (0.520 g); mp 102.2−105.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J = 8.4 Hz, 4H), 7.72 (s, 4H), 7.31 (dd, J = 8.4, 1.8 Hz, 4H), 7.03 (d, J = 1.8 Hz, 4H), 6.98 (d, J = 1.5 Hz, 4H), 5.37 (s, 8H), 4.09 (t, J = 6.9 Hz, 8H), 1.78 (quint, J = 7.5 Hz, 8H), 1.33 (quint, J = 7.5 Hz, 8H), 0.93 (t, J = 7.2 Hz, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 181.2, 133.9, 133.0, 132.8, 129.0, 127.5, 125.9, 121.4, 121.3, 55.7, 52.0, 33.4, 19.7, 13.7; IR (KBr) 3469, 3145, 3117, 3092, 2955, 2922, 2868, 2370, 2328, 1684, 1636, 1559, 1515, 1457, 1417, 1373, 1229, 1180, 1104, 962, 845, 737, 666, 500, 470, 458. Anal. Calcd for $C_{52}H_{64}Ag_4Br_4N_8$: C, 40.24; H, 4.16; N, 7.22. Found: C, 40.15; H, 4.20; N, 7.09.

*General Procedure for Synthesis of Dinuclear Silver-Carbene Complex Hexafluorophosphate Salts (**6a**, **6c**).* Ag_2O (0.75 mmol) and *n*-Bu_4NPF_6 (5 μmol) were added to a solution of the imidazolium hexafluorophosphate **4** (0.5 mmol) in CH_2Cl_2 (50 mL). The mixture was stirred for 26−41 h under dark conditions after addition of NaOH(aq) (1 M, 3 mL). The reaction was monitored by TLC and ^{1}H NMR. The mixture was filtered through Celite, and the filtrate was evaporated to give the crude product. The product was further purified by recrystallization (CH_2Cl_2/Et_2O).

*[Napht-n-Bu$_2$]$_2$Ag$_2$-2PF$_6$ (**6a**):* colorless solid; yield 84% (0.319 g); mp >300 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.81 (d, J = 8.7 Hz, 4H), 7.63 (s, 8H), 7.48 (t, J = 7.5 Hz, 4H), 7.23 (d, J = 7.8 Hz, 8H), 7.15 (s, 4H), 7.01 (d, J = 8.7 Hz, 4H), 4.95 (s, 8H), 2.17 (quint, J = 6.9 Hz, 8H), 1.06 (d, J = 6.9 Hz, 24H), 0.85 (d, J = 6.9 Hz, 24H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 181.1 (dd, $J_{C-^{107}Ag}$ = 181 Hz, $J_{C-^{109}Ag}$ = 211 Hz), 145.2, 135.3, 134.6, 132.2, 131.8, 130.5, 128.6, 125.5, 125.4, 125.0, 124.9, 123.3, 53.5, 28.1, 24.7, 23.6; IR (KBr) 3170, 2964, 2931, 2871, 1640, 1559, 1508, 1473, 1417, 1386, 1364, 1316, 1252, 1183, 1105, 1059, 959, 843, 760, 689, 623, 557, 472. Anal. Calcd for $C_{84}H_{96}Ag_2F_{12}N_8P_2$: C, 58.54; H, 5.61; N, 6.50. Found: C, 58.25; H, 5.54; N, 6.36.

*[Napht-Cy$_2$]$_2$Ag$_2$-2PF$_6$ (**6c**):* colorless solid; yield 76% (0.268 g); mp 203.5−208.2 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.83 (d, J = 9.0 Hz, 4H), 7.57 (m, 8H), 7.31 (s, 8H), 5.15 (s, 8H), 4.13 (t, J = 11 Hz, 4H), 1.82−1.53 (m, 28H), 1.16−1.04 (m, 12H); ^{13}C NMR (150 MHz, DMSO-d_6) δ 178.4, 135.8, 132.3, 131.8, 128.4, 125.7, 125.3, 122.3, 119.9, 60.8, 53.9, 34.0, 25.0, 24.5; IR (KBr) 3447, 3173, 3150, 3048, 2934, 2857, 2667, 2363, 2344, 2335, 2324, 1616, 1515, 1449, 1421, 1242, 1181, 1114, 1037, 989, 837, 740, 668, 559. Anal. Calcd for $C_{60}H_{72}Ag_2F_{12}N_8P_2$: C, 51.08; H, 5.14; N, 7.94. Found: C, 50.79; H, 5.11; N, 7.83.

Synthesis of Dinuclear Silver-Carbene Complex Hexafluorophosphate Salt (6a) from 5a (Scheme 2). Compound **5a** (0.488 g, 0.25 mmol) was suspended in CH_2Cl_2 (60 mL), and KPF_6 (0.92 g, 5 mmol) was addded in one portion. After being stirred overnight, the bluish mixture was filtered through Celite and evaporated. A quantitative amount of **6a** was obtained.

General Procedure for Synthesis of Dinuclear Palladium-Carbene Complexes (Scheme 3). A dry CH_2Cl_2 solution of complex **6**, Pd complex [$Pd(MeCN)_2Cl_2$ or $Pd(cod)Br_2$], and ammonium salt (*n*-Bu_4NBr or Et_4NCl) was stirred at rt for 7−11 h under Ar. The reaction was monitored by TLC. After completion of the reaction, the mixture was filtered through Celite and the volatiles were removed under vacuum to give the crude product. The crude product was passed through short silica gel column and purified by recrystallization.

*[Napht-Ipr$_2$]$_2$Pd$_2$-Cl$_4$ (**7a**).* This compound was prepared following the general procedure from complex **6a** (86 mg, 0.05 mmol), $Pd(MeCN)_2Cl_2$ (31 mg, 0.12 mmol), and Et_4NCl (25 mg, 0.15 mmol) in CH_2Cl_2 (80 mL). The product was purified by recrystallization (acetone/hexane). Pale yellow solid: yield 73% (58.3 mg); mp 280 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, J = 8.5 Hz, 4H), 7.59 (s, 4H), 7.35 (t, J = 7.5 Hz, 4H), 7.10 (d, J = 7.5 Hz, 12H), 6.71 (d, J = 1.5 Hz, 4H), 6.67 (d, J = 1.5 Hz, 4H), 5.62 (s, 8H), 2.70 (quint, J = 6.5 Hz, 8H), 0.96 (d, J = 6.5 Hz, 24H), 0.90−0.89 (d, J = 7.0 Hz, 24H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.0, 146.3, 135.1, 134.0, 132.6, 132.1, 129,4, 128.2, 126.6, 126.0, 124.1, 123.6, 120.6, 54.0, 28.1, 26.3, 22.9; IR (KBr) 3452, 3169, 3138, 3066, 2965, 2922, 2868, 2365, 1938, 1638, 1514, 1458, 1417, 1385, 1364, 1292, 1251, 1222, 1180, 1120, 1060, 958, 936, 899, 840, 802, 757, 730, 703, 667, 632, 607, 590, 577, 547, 539, 529, 517, 500, 470, 463, 440, 410; HRMS-ESI (m/z) $[M + Na]^+$ calcd for for $C_{84}H_{96}Cl_4N_8Pd_2Na$, 1591.4494; found, 1591.4458. Anal. Calcd for $C_{84}H_{96}Cl_4N_8Pd_2$: C, 64.16; H, 6.15; N, 7.13. Found: C, 63.99; H, 6.20; N, 7.12.

*[Napht-Cy$_2$]$_2$Pd$_2$-Cl$_4$ (**7c**).* Complex **6c** (0.28 g, 0.2 mmol), $Pd(MeCN)_2Cl_2$ (0.12 g, 0.48 mmol), and Et_4NCl (0.10 g, 0.60 mmol) in CH_2Cl_2 (320 mL). were used to prepare this complex following the general procedure. The product was purified by recrystallization ($CHCl_3$/hexane). Pale yellow solid: yield 79% (0.199 g); mp >300 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, J = 8.4 Hz, 4H), 7.43 (s, 4H), 7.09 (d, J = 8.4 Hz, 4H), 6.84 (d, J = 1.2 Hz, 4H), 6.62 (d, J = 1.8 Hz, 4H), 5.38 (s, 8H), 5.29−5.30 (m(br), 4H), 2.47−2.48 (m, 8H), 1.95−1.97 (m, 8H), 1.80 (d, J = 7.8 Hz, 4H), 1.47−1.63 (m, 16H), 1.24−1.28 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 134.3, 132.6, 132.1, 128.1, 126.2, 125.7, 121.2, 117.0, 59.9, 53.7, 34.1, 25.9, 25.5; IR (KBr) 3471, 3122, 3089, 2933, 2854, 2676, 2365, 2328, 1636, 1559, 1516, 1452, 1425, 1379, 1224, 1182, 990, 894, 840, 819, 728, 697, 668, 629, 577, 569, 560, 530, 518, 507, 500, 488, 480, 470, 459, 440, 430, 422. Anal. Calcd for $C_{60}H_{72}Cl_4N_8Pd_2$: C, 57.20; H, 5.76; N, 8.89. Found: C, 56.92; H, 5.65; N, 8.67.

*[Napht-Ipr$_2$]$_2$Pd$_2$-Br$_4$ (**8a**).* This compound was prepared from complex **6a** (43 mg, 0.025 mmol), $Pd(cod)Br_2$ (19 mg, 0.05 mmol), and *n*-Bu_4NBr (16 mg, 0.05 mmol) following the general procedure. X-ray diffraction quality crystals were obtained by layering an acetone solution with hexane. Pale yellow solid: yield 35% (15.6 mg); mp 272.0−275.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 4H), 7.63 (d, J = 8.0 Hz, 4H), 7.34 (t, J = 7.5 Hz, 4H), 7.12 (d, J = 8.5 Hz, 4H), 7.08 (d, J = 8.0 Hz, 8H), 6.71 (d, J = 2.0 Hz, 4H), 6.70 (d, J = 2.0 Hz, 4H), 5.65 (s, 8H), 2.81 (quint, J = 6.5 Hz, 8H), 0.96 (d, J = 7.0 Hz, 24H), 0.88 (d, J = 6.5 Hz, 24H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.3, 146.6, 135.2, 133.7, 132.6, 132.2, 129.4, 128.2, 127.1, 126.3, 124.6, 123.7, 120.7, 54.7, 28.2, 26.4, 23.1; IR (KBr) 3429, 3136, 3061, 3029, 2963, 2928, 2867, 2372, 1702, 1637, 1562, 1543, 1518, 1508, 1467, 1415, 1384, 1362, 1291, 1249, 1214, 1180, 1121, 1098, 1059, 959, 932, 842, 802, 758, 727, 702, 628, 473, 419; HRMS-ESI (m/z) $[M - Br]^+$ calcd for $C_{84}H_{96}Br_3N_3Pd_2$, 1667.3385; found, 1667.3328. Anal. Calcd for $C_{84}H_{102}Br_4N_8O_3Pd_2$ (**8a**·$3H_2O$): C, 55.81; H, 5.75; N, 5.96. Found: C, 55.92; H, 5.70; N, 6.21.

Synthesis of Dinuclear Palladium-Carbene Complexes (Scheme 4). *[Napht-n-Bu$_2$]$_2$Pd$_2$-I$_4$ (**9b**).* A dry CH_2Cl_2 (40 mL) solution of complex **5b** (78 mg, 0.05 mmol) and $Pd(cod)Cl_2$ (29 mg, 0.1 mmol) was stirred at rt for 24 h under Ar. The reaction was monitored by TLC and ^{1}H NMR. After completion of the reaction, the mixture was filtrated through Celite and the volatiles were removed under vacuum. The remaining solid was washed with Et_2O and dried under vacuum. The resulting solid and NaI (150 mg, 1 mmol) in CH_2Cl_2 (10 mL) were stirred for 24 h at rt, then filtered through Celite and evaporated to give the crude product. The crude product was purified by recrystallization (CH_2Cl_2/hexane). X-ray diffraction quality crystals were obtained from

a CH_2Cl_2 solution after the Pd complex was dissolved in CH_2Cl_2 and then kept at rt. Pale yellow solid: yield 71% (55 mg); mp 277.0−282.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (s, 4H), 7.51 (d, J = 7.8 Hz, 4H), 7.08 (dd, J = 1.2, 8.1 Hz, 4H), 6.83 (d, J = 1.8 Hz, 4H), 6.65 (d, J = 1.8 Hz, 4H), 5.24 (s, 8H), 4.38 (t, J = 7.8 Hz, 8H), 2.02 (quint, J = 7.5 Hz, 8H), 1.43 (quint, J = 7.5 Hz, 8H), 0.99 (d, J = 7.2 Hz, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.9, 133.5, 132.5, 132.2, 128.3, 127.0, 126.6, 121.9, 121.0, 54.9, 51.7, 32.2, 20.1, 13.7; IR (KBr) 3447, 3161, 3126, 2958, 2928, 2869, 2369, 1637, 1560, 1543, 1517, 1459, 1417, 1375, 1309, 1224, 1177, 1129, 1031, 963, 898, 850, 796, 756, 722, 696, 473. Anal. Calcd for $C_{52}H_{64}I_4N_8Pd_2$: C, 41.05; H, 4.24; N, 7.36. Found: C, 41.26; H, 4.30; N, 7.07.

General Procedure for the Mizoroki−Heck Reaction (Tables 3 and 4). To a solution of the Pd complex in dry DMF (2.5 mL) were added aryl halide (1 mmol), sodium formate (6.8 mg, 0.1 mmol), *i*-Pr_2NEt (0.19 mL, 1.1 mmol), and *n*-butyl acrylate (0.2 mL, 1.4 mmol) under an argon atmosphere. After being heated at the indicated temperature for the specified period, the reaction mixture was cooled to rt. The solution was diluted with CH_2Cl_2 and washed with water three times. The organic layer was dried over Mg_2SO_4 and evaporated. The residue was purified by silica gel chromatography (CH_2Cl_2/hexane).

■ ASSOCIATED CONTENT

Supporting Information. Experimental procedures, characterization data, copies of NMR spectra, and X-ray analysis data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*Tel: +81-3-5228-8715. E-mail: ssaito@rs.kagu.tus.ac.jp.

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