Synthesis and Characterization of Proximal Dinuclear Complexes of Palladium Supported by 2,6-Bis(arylimino)phenoxy (aryl = 2,6-diisopropylphenyl and 2,4,6-tri-*tert*-butylphenyl) and 3,6-Bis(imino(2,6-diisopropylphenyl))pyridazine Ligands

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Two kinds of binucleating ligands, 2,6-bis(arylimino)phenoxy (**1a**: aryl = 2,6-diisopropylphenyl; **1b**: aryl = 2,4,6-tri-*tert*-butylphenyl) and 3,6-bis(imino(2,6-diisopropylphenyl))pyridazine (**2**), were prepared, and their proximal complexation with two palladium atoms was studied. Treatment of the sodium compounds of **1a**,**b** with 2 equiv of $PdCl_2(PhCN)_2$ and PdMeCl(cod) afforded the corresponding homobimetallic complexes, [2,6-bis(arylimino)phenoxy][RPd(μ-Cl)PdR] (**4a**: R = Cl, aryl = 2,6-diisopropylphenyl; **4b**: R = Cl, aryl = 2,4,6-tri-*tert*-butylphenyl; **7a**: R = Me, aryl = 2,6-diisopropylphenyl; **7b**: R = Me, aryl = 2,4,6-tri-*tert*-butylphenyl), whose structures were characterized spectroscopically and crystallographically. In the reaction between the sodium compound of **1a** with 1 equiv of $PdCl_2(PhCN)_2$, we detected the NaCl adduct of mononuclear palladium species **5a**, which, upon release of NaCl, formed a dimeric complex, ([2,6-bis(2,6-diisopropylphenylimino)phenoxy](PdCl])$_2$ (**4a**), as confirmed by X-ray analysis. Complexation of **2** with 2 equiv of $PdCl_2(PhCN)_2$ and PdMeCl(cod) in the presence of 1 equiv of $AgBF_4$ resulted in the formation of the corresponding cationic complexes ([3,6-bis(imino(2,6-diisopropylphenyl))pyridazine][RPd(μ-Cl)PdR])(BF_4) (**9a**: R = Cl; **9b**: R = Me), whose RPd(μ-Cl)PdR skeletons (R = Cl and Me) were revealed spectroscopically and crystallographically.

Introduction

Assembled metal clusters supported by well-designed multidentate ligands have recently attracted considerable interest because of their potential catalytic applications to any organic transformation.[1−8] Although many compounds of main group elements act as ambifunctional cooperative catalysts, dinuclear complexes bearing two transition metal centers at the proximal positions are anticipated to be one of the most fundamental entities to exhibit a cooperative effect, accelerating catalytic activity, improving selectivity, and promoting unexpected reactivity, and not a simple extension of a single metal complex. This recent development is due to a rational design of different types of ligands to fix two metal centers in proximity to cooperatively catalyze any targeted organic transformation, through application of the unique bridging ability of hydride and sulfur atoms for dinuclear ruthenium systems used to catalyze unique transformations of propargyl substrates[9] and dehydrogenative coupling of substituted pyridines.[10] The clear advantage of dinuclear complexes was demonstrated by Stanley et al. in the highly regioselective hydroformylation of olefins catalyzed by a dirhodium complex bridged by a tetraphosphine ligand.[11,12] Another phosphine-based ligand system was reported by Tsukada and Inoue whose dinuclear palladium catalysts, supported by a unique *N*,*N*′-bis[(2-diphenylphosphino)phenyl]-formamidate ligand, catalyzed *cis*-hydroarylation of alkynes with unactivated arenes in the presence of trialkylborane.[13,14] Pyrazolate ligands with armed functional groups have been used to support two metal centers.[15,16] Recently Akita et al. developed a unique 3,5-bis((diphenylphosphino)methyl)pyrazolato) ligand system for stoichiometrically activating alkyne substrates.[17−19] Some binucleating bisphenoxy ligands have been designed to

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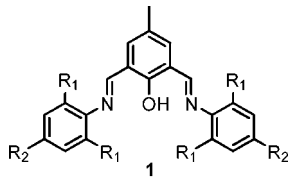
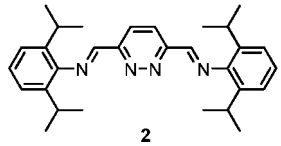
proximally bind two aluminum atoms.[6−8,20] These developments prompted us to design and prepare new proximal ligand systems to maintain the two metal centers at one side of the ligand. Our strategy was based on the use of a standard two-armed phenoxy moiety[5,21−27] and the skeleton of pyridazine modified with two arms,[28−30] and we herein report the synthesis and characterization of dinuclear palladium complexes of 2,6-di(aryliminomethyl)-4-methylphenol (aryl = 2,6-diisoproplyphenyl (**1a**)[31] and 2,4,6-tri-*tert*-butylphenyl (**1b**)) and 3,6-bis(imino(2,6-diisopropylphenyl))pyridazine (**2**).



1

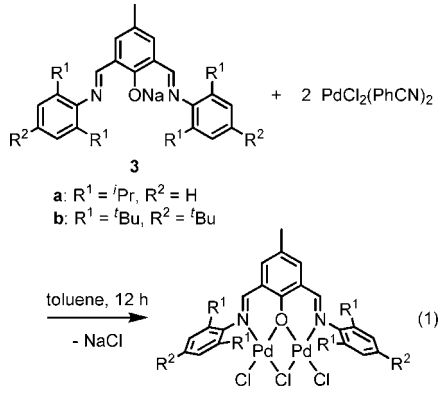
a: $R^1 = {}^i\text{Pr}$, $R^2 = H$
b: $R^1 = {}^t\text{Bu}$, $R^2 = {}^t\text{Bu}$



2

Results and Discussion

Synthesis of Dinuclear Palladium Complexes of 2,6-Bis(arylimino)phenoxy Ligands. Reaction of **3a**, which was derived from **1a** and NaH in THF, with 2 equiv of $PdCl_2(PhCN)_2$ in toluene afforded dinuclear palladium complex **4a** as an orange powder (eq 1). In the same procedure, palladium complex **4b** was obtained by the reaction of **3b** and 2 equiv of $PdCl_2(PhCN)_2$.



3

a: $R^1 = {}^i\text{Pr}$, $R^2 = H$
b: $R^1 = {}^t\text{Bu}$, $R^2 = {}^t\text{Bu}$

4

a: $R^1 = {}^i\text{Pr}$, $R^2 = H$
b: $R^1 = {}^t\text{Bu}$, $R^2 = {}^t\text{Bu}$

Complexes **4a** and **4b** were characterized by spectral data and elemental analysis along with single-crystal X-ray analyses. In the FAB-MS spectrum of **4a**, a parent ion peak was observed. In the reaction of **3a** and $PdCl_2(PhCN)_2$, two new resonances due to CH_3 in the isopropyl groups of **4a** appeared at δ 1.48 and 1.15. The formation of the dinuclear palladium complex **4a** resulted in the differentiation of nonequivalent CH_3 in the isopropyl groups; one was oriented toward the imine moiety and the other opposite of it. The resonance due to the two imine protons overlapped with the aromatic signals. The ^1H NMR spectrum of **4b** was also consistent with the symmetric pattern due to the formation of the dinuclear palladium, displaying a singlet due to the imine proton at δ 7.50 and two singlets due to two *tert*-butyl groups at δ 1.69 and 1.23.

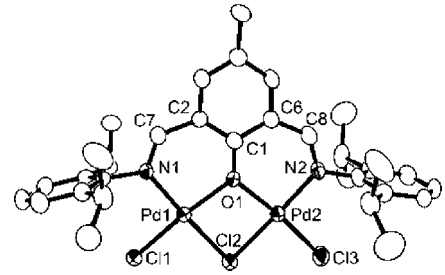


Figure 1. Structure of complex **4a** with the numbering scheme. Cocrystallized CH_2Cl_2 molecule and hydrogen atoms are omitted for clarity. One of the two molecules in the asymmetric unit.

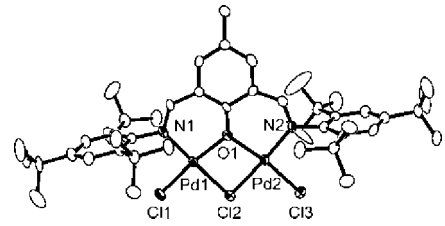


Figure 2. Structure of complex **4b** with the numbering scheme. Hydrogen atoms are omitted for clarity.

Crystals of complexes **4a** and **4b** suitable for X-ray analysis were grown from a mixture of dichloromethane and hexane. Figures 1 and 2 show the molecular structures of complexes **4a** and **4b**, respectively, and the selected bond lengths and angles of **4a** and **4b** are summarized in Table 1. Complexes **4a** and **4b** are isomorphic except for the substituents at the aromatic moieties bound to the nitrogen atoms. The two palladium centers are doubly bridged by the oxygen atom of the ligand and the chlorine atom. In complexes **4a** and **4b**, each geometry around

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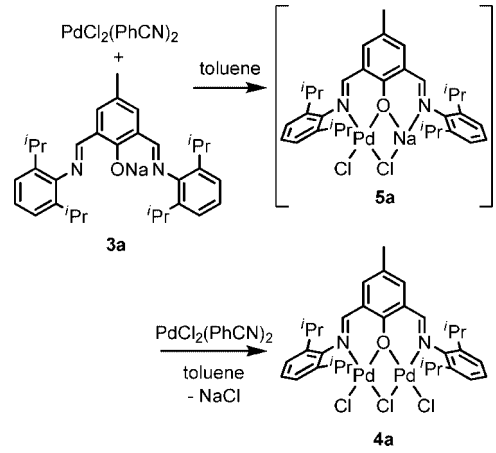
Table 1. Selected Bond Distances (Å) and Angles (deg) of 4

	4a	4b
Pd1−N1	1.977(6)	1.997(5)
Pd2−N2	2.012(6)	2.018(4)
Pd1−O1	2.063(4)	2.046(4)
Pd2−O1	2.042(5)	2.065(4)
Pd1−Cl1	2.2650(16)	2.2677(15)
Pd2−Cl3	2.2493(19)	2.2716(15)
Pd1−Cl2	2.3125(18)	2.3409(15)
Pd2−Cl2	2.3219(17)	2.3300(15)
C1−O1	1.302(7)	1.333(7)
N1−Pd1−O1	93.0(2)	93.55(18)
N2−Pd2−O1	92.9(2)	93.96(17)
N1−Pd1−Cl1	93.54(16)	93.70(14)
N2−Pd2−Cl3	93.42(18)	93.19(14)
O1−Pd1−Cl2	83.57(13)	82.67(12)
O1−Pd2−Cl2	83.80(13)	82.54(11)
Cl1−Pd1−Cl2	89.92(6)	90.24(5)
Cl3−Pd2−Cl2	90.07(7)	90.40(5)
Pd1−O1−Pd2	103.97(19)	105.63(18)
Pd1−Cl2−Pd2	88.50(6)	89.03(5)
C1−O1−Pd1	128.3(4)	127.1(3)
C1−O1−Pd2	127.3(4)	127.0(3)

the two palladium atoms is slightly distorted square planar. In complex **4a**, the geometries around two palladium centers are essentially the same except for the distance of the Pd−N bond: the distance of Pd(1)−N(1) [1.977(6) Å] is slightly shorter than that of Pd(2)−N(2) [2.012(6) Å]. The terminal Pd−Cl distances of Pd(1)−Cl(1) [2.2677(15) Å] and Pd(2)−Cl(3) [2.2716(15) Å] are shorter than those of the bridged Pd−Cl distances of Pd(1)−Cl(2) [2.3409(15) Å] and Pd(2)−Cl(2) [2.3300(15) Å].[32] A similar trend was observed in **4b**.

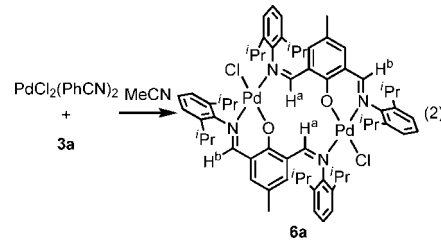
To gain insight into the reaction pathways of **3a** and **3b** with 2 equiv of $PdCl_2(PhCN)_2$, a controlled experiment was conducted. As outlined in Scheme 1, complex **3a** reacted with 1 equiv of $PdCl_2(PhCN)_2$ in *toluene* at room temperature to give the mononuclear compound **5a**, which further reacted with another equivalent of $PdCl_2(PhCN)_2$ to give the dinuclear palladium complex **4a** in quantitative yield. Because complex **5a** was coordinatively unsaturated, we anticipated that the coordination site was occupied by a salt, NaCl, with a bridged phenolic oxygen atom. The partial contribution of the radical character of the ligand, due to the partial electron transfer

Scheme 1. Proposed Reaction Mechanism



between palladium metal and the noninnocent redox-active ligand **1**, may explain the paramagnetic nature of **5a**, as we observed very broad signals due to the presence of paramagnetic species in the ^{1}H NMR spectrum of *in situ* generated **5a** in $CDCl_3$.

To elucidate the structure of **5a**, another controlled experiment was conducted. The sodium compound **3a** reacted with 1 equiv of $PdCl_2(PhCN)_2$ in *acetonitrile* at room temperature gave the new dimer complex **6a** (eq 2) after the release of NaCl. The isolated complex **6a** did not react with another equivalent of $PdCl_2(PhCN)_2$, presumably due to the stability of the dimer structure, which was in sharp contrast to the observation that the one-pot reaction of **3a** with 2 equiv of $PdCl_2(PhCN)_2$ in acetonitrile gave the dinuclear palladium complex **4a** in quantitative yield. Complex **6a** was characterized by ^{1}H and ^{13}C NMR, mass spectroscopies, and a single-crystal X-ray analysis. Similarly, a palladium enolate complex readily dimerized to form a stable dinuclear complex ([N $\hat{N}$]$PdCH_2C(=O)OCH_3)_2$ (N $\hat{N}$ = 1-[1-(5-methylpyrrole-2-yl)ethylidne]amino-2,6-diisopropylbenzene) bridged by the *C*,*O*-enolato groups.[33]



In the ^{1}H NMR spectrum of **6a** in $CDCl_3$, four doublets (δ 1.40, 1.35, 1.08, and 0.97) assigned to protons of CH_3 in the isopropyl group were observed. Resonances due to two nonequivalent imine protons (H^a or H^b) appeared at δ 10.28 and in the aryl region, respectively. The IR spectrum showed two sharp bands at 1635 and 1617 cm^{-1}, due to the C=N stretching vibration.

Crystals of **6a** suitable for an X-ray analysis were grown from hexane at room temperature. Figure 3 shows the molecular structure of **6a**, and selected bond lengths and angles of **6a** are summarized in Table 2. In the solid state, there are two types of hydrogen bonds between the hydrogen atom in the ethylene group and the hydrogen atom in the phenolic oxygen [O(1)−H(7) = 2.27 Å and O(1*)−H(7) = 2.09 Å]. The sum of the van der

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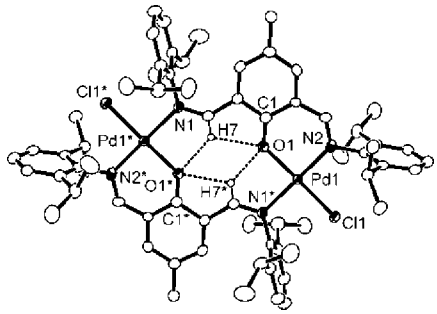


Figure 3. Structure of complex **6a** with the numbering scheme. Hydrogen atoms are omitted for clarity. One of the two moleclues in the asymmetric unit. Symmetry transformations used to generate equiv atoms (atom name *): $-x$, $-y$, $-z$.

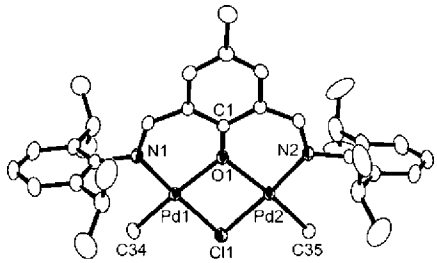


Figure 4. Structure of complex **7a** with the numbering scheme. Cocrystallized hexane molecule and hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) of 6a

Pd1−N1*	2.088(4)	Pd1−N2	2.023(4)
Pd1−O1	2.019(4)	Pd1−Cl1	2.2850(14)
C1−O1	1.304(6)		
N1*−Pd1−O1	88.33(16)	N2−Pd1−O1	90.71(16)
N1*−Pd1−Cl1	90.18(12)	N2−Pd1−Cl1	90.81(13)
C1−O1−Pd1	128.7(3)		

Hydrogen Bonding Geometry (Å and deg)

D−H---A	D−H	H---A	D---A	D-H---A
C7−H7---O1	0.95(2)	2.27(2)	2.708(6)	107.2
C7−H7---O1*	0.95(2)	2.09(2)	2.795(6)	129.6

Table 3. Selected Bond Distances (Å) and Angles (deg) of 7a

Pd1−N1	2.0217(16)	Pd2−N2	2.0189(16)
Pd1−O1	2.1243(13)	Pd2−O1	2.1294(13)
Pd1−Cl1	2.3453(5)	Pd2−Cl1	2.3398(5)
Pd1−C34	2.006(2)	Pd2−C35	2.0220(19)
C1−O1	1.300(2)		
N1−Pd1−O1	91.16(6)	N2−Pd2−O1	90.62(6)
O1−Pd1−Cl1	84.43(4)	O1−Pd2−Cl1	84.45(4)
Cl1−Pd1−C34	91.03(6)	Cl1−Pd2−C35	90.35(6)
C34−Pd1−N1	93.45(8)	C35−Pd2−N2	94.58(8)
Pd1−O1−Pd2	101.34(5)	Pd1−Cl1−Pd2	89.219(17)
C1−O1−Pd1	127.35(12)	C1−O1−Pd2	127.19(12)

Waals radii of the O and H atoms (2.72 Å)[34] is significantly longer than the observed O−H distances, indicating that Ha (= H7) bridges two oxygen atoms through two hydrogen bonds, which stabilizes the dimer structure of **6a**. The C(1)═C(2)−C(7)═N(1) sequence adopted an *s-trans*conformation, whereas that of C(1)═C(6)−C(21)═N(2) was *s-cis*, despite the fact that each C═N double bond has an *E* configuration. The geometry around the palladium atom is a slightly distorted square planar.

(34) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

Treatment of **3a** with 2 equiv of (cod)PdMeCl in toluene afforded dinuclear dimethyl palladium complex **7a** as a yellow powder in quantitative yield. Based on ^{1}H and ^{13}C NMR spectral data, dinuclear palladium complex **7a** has two methyl groups bound to each palladium atom, and the chlorine atom and oxygen atom of the phenolic spacer act as bridging ligands: methyl protons and methyl carbons appeared at δ_H 0.12 and δ_C −2.1, respectively, indicating that each methyl group is bound directly to each palladium atom as a terminal ligand. Complex **7b** was also prepared according to the same procedure as **7a** in quantitative yield. The μ-Cl bridge is quite stable, and the chloride could not be displaced even upon treatment with $AgBF_4$.

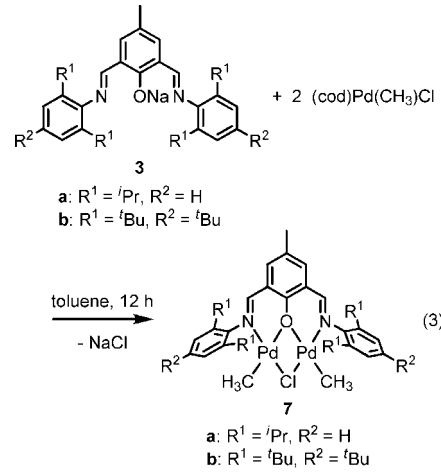


Figure 4 shows the molecular structure of dinuclear methyl palladium complex **7a**, and selected bond lengths and angles are summarized in Table 3. The terminal Pd−C distance of Pd(1)−C(34) [2.006(2) Å] is shorter than that of Pd(2)−C(35) [2.0220(19) Å]. Other bond distances around Pd(1) [2.0217(16), 2.1243(13), and 2.3453(5) Å] for Pd(1)−N(1), Pd(1)−O(1), and Pd(1)−Cl(1), respectively, are almost the same as the bond distances around Pd(2). Although the Pd(1)−Cl(1) distance of **7a** [2.3453(5) Å] is longer than that of **4a** [2.3125 (18) Å], the C(1)−O(1) distance of **7a** [1.300(2) Å] is the same as that of **4a** [1.302(7) Å]. These features are likely due to the increased electron density at each palladium atom with a methyl group in complex **7a**.

Reactions of **3a** with platinum compounds $PtCl_2(PhCN)_2$ and $PtCl_2(MeCN)_2$ and a nickel compound, $NiCl_2(PPh_3)_2$, did not give the desired dinuclear products under the same reaction conditions as palladium; however, in the case of $NiClPh(PPh_3)_2$, the reaction with **3a** gave complex **8** as a green powder (eq 4). Bis-chelated nickel complexes with this type of *O,N*-ligand, similar to complex **8**, are thermodynamically favored, and their formation has been discussed in relation to ethylene polymerization catalysts.[35−37]

Complex **8** was crystallized from toluene, and its structure was measured by X-ray single-crystal structure determination. The ^{1}H NMR spectrum of **8** in $CDCl_3$ is consistent with this structure in the solid state. The four diastereotopic protons in methyl groups are observed at δ 1.43, 1.32, 1.19, and 1.00, and

(35) Connor, E. F.; Younkin, T. R.; Henderson, J. I.; Waltman, A. W.; Grubbs, R. H. *Chem. Commun.* **2003**, 2272.

(36) Foley, S. R.; Stockland, R. A., Jr.; Shen, H.; Jordan, R. F. *J. Am. Chem. Soc.* **2003**, *125*, 4350.

(37) Waltman, A. W.; Younkin, T. R.; Grubbs, R. H. *Organometallics* **2004**, *23*, 5121.

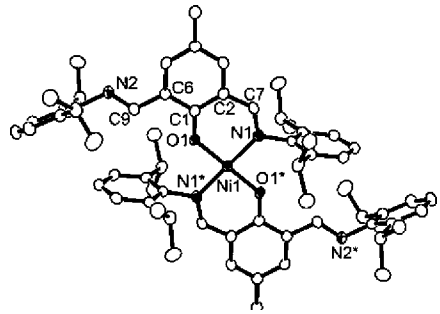


Figure 5. Structure of complex **8** with the numbering scheme. Hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms (atom name *): $-x$, $-y$, $-z$.

Table 4. Selected Bond Distances (Å) and Angles (deg) of 8

Ni1−N1	1.896(2)	Ni1−O1	1.8588(18)
C1−O1	1.309(3)		
N1−Ni1−O1	93.13(9)	N1−Ni1−O1*	86.87(9)
Ni1−O1−C1	130.15(18)		

two imine protons are also observed at δ 7.96 and the aromatic region, respectively.

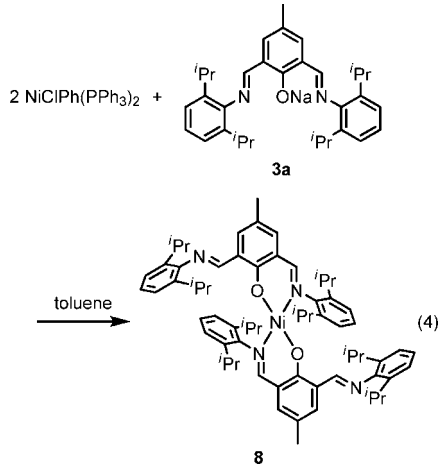
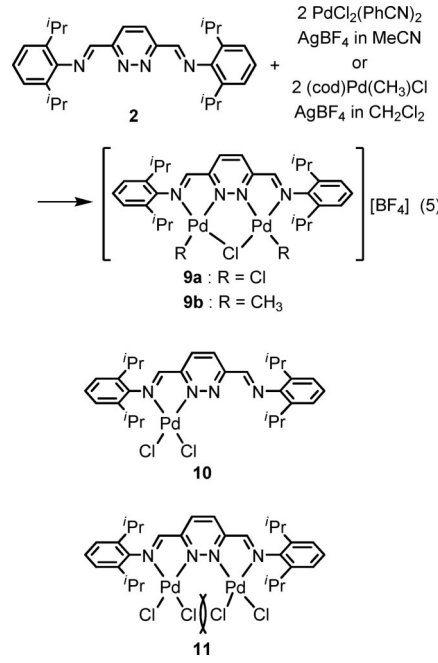


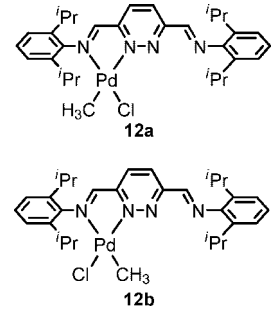
Figure 5 shows the molecular structure of complex **8**, and its selected bond lengths and angles are summarized in Table 4. Complex **8** adopts a distorted square-planar geometry, as observed for some related nickel complexes.[35,36] The distance of Ni(1)−O(1) [1.8588(16) Å] is shorter than that of Ni(1)−N(1) [1.896(2) Å], because nickel has strong oxophilicity. In the solid state, the C(1)═C(2)−C(7)═N(1) sequence adopts an *s-trans* conformation, whereas that of C(1)═C(6)−C(9)═N(2) was *s-cis*, although each C═N double bond has an *E* configuration. The geometry around the nickel atom is square-planar.

Synthesis of Dinuclear Complexes Supported by 3,6-Bis(imino(2,6-diisopropylphenyl))pyridazine (2). Treatment of **2** with 2 equiv of $PdCl_2(PhCN)_2$ in the presence of 1 equiv of $AgBF_4$ in CH_3CN afforded cationic dinuclear complex **9a** in quantitative yield (eq 5). Similarly, reaction of **2** with 2 equiv of PdClMe(cod) in the presence of 1 equiv of $AgBF_4$ in dichloromethane at −78 °C also afforded cationic complex **9b** in quantitative yield. Complexes **9a** and **9b** were characterized by ^{1}H NMR, ^{13}C(^{1}H) NMR, combustion analysis, and X-ray analyses. These reactions required 1 equiv of $AgBF_4$; otherwise, the reaction resulted in a complicated mixture and no products were obtained.

In the control experiment, we first perfomed the reaction of **2** with 1 equiv of $PdCl_2(PhCN)_2$ in the absence of $AgBF_4$ to give mononuclear complex **10**, to which the second $PdCl_2$ did not coordinate due to steric congestion between the two chlorine atoms in the possible complex **11**. Thus, it is likely that the abstraction of one chlorine atom from complex **10** by $AgBF_4$ opened a coordination site and then the second $PdCl_2$ moiety occupied the proximal position to form the chlorine-bridged dinuclear skeleton. Similarly, proximal dinuclear complexation with different kinds of supporting ligands is hampered by an intramolecular contact between the halides bound to the metal and the second halo metal unit.[23−25,27,38]



Similar treatment of **2** with 1 equiv of PdClMe(cod) at room temperature produced a mixture of two complexes, **12a** and **12b** (major/minor = 5:2). Treatment of **12a** and **12b** with 1 equiv of PdClMe(cod) in the presence of 1 equiv of $AgBF_4$ in dichloromethane at −78 °C resulted in the quantitative formation of complex **9b**. When this reaction was conducted at room temperature, we obtained a complicated mixture containing a black precipitate. The intermediate cationic species derived from **12a** and **12b** were thermally unstable at room temperature.



Complex **9b** was crystallized from a mixture of dichloromethane and hexane. Figure 6 shows the cationic part of the dinuclear palladium complex **9b**, and selected bond distances and angles are summarized in Table 5. The two palladium atoms are confirmed to be in the proximal positions bridged by a chloride anion; the skeleton of Pd1−Cl1−Pd2 has distances of 2.3723(13) Å for Pd1−Cl1 and 2.3733(12) Å for Pd2−Cl1 and an angle of 100.46(5)°. The difference in the Pd−CH_3 bond

(38) Tsukada, N.; Sato, T.; Mori, H.; Sugawara, S.; Kabuto, C.; Miyano, S.; Inoue, Y. *J. Organomet. Chem.* **2001**, *627*, 121.

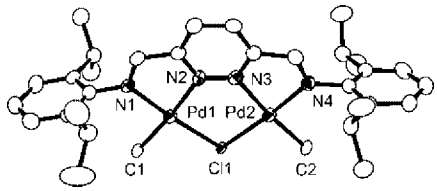


Figure 6. Cationic part of complex **9b**. All hydrogen atoms, solvent molecules, and tetrafluoroborate anion are omitted for clarity.

Table 5. Selected Bond Distances (Å) and Angles (deg) of 9b

Pd1−C1	2.058(5)	Pd1−Cl1	2.3723(13)
Pd1−N1	2.048(5)	Pd1−N2	2.096(5)
Pd2−C2	2.055(6)	Pd2−Cl1	2.3733(12)
Pd2−N4	2.049(5)	Pd2−N3	2.093(5)
C1−Pd1−Cl1	90.64(18)	C1−Pd1−N1	95.3(2)
Cl1−Pd1−N2	96.15(15)	N1−Pd1−N2	77.8(2)
C2−Pd2−Cl1	90.52(15)	C2−Pd2−N4	95.6(2)
Cl1−Pd2−N3	95.80(13)	N3−Pd2−N4	78.02(19)
Pd1−Cl1−Pd2	100.46(5)	Pd1−N2−N3	123.2(4)
Pd2−N3−N2	124.4(4)		

distance between **9b** and **7a** is attributed to the *trans* influence of the pyridazine ring and phenoxide ligands.

Conclusion

We report the syntheses of dinuclear palladium complexes supported by bis(iminomethyl)phenolate and 3,6-bis(imino(2,6-diisopropylphenyl))pyridazine ligands, which were designed to act as proximal ligands. Two palladium atoms were bridged by a chlorine atom, forming an R−Pd(μ-Cl)Pd−R skeleton where R = Cl and CH_3 for both ligand systems. For the phenolate ligands, the dinuclearization proceeds through the NaCl adduct **5a** and removal of the salt led to the formation of dimer compounds **4a** and **4b**. In the case of the pyridazine ligand, two palladium metals successively coordinated to the ligand only in the presence of $AgBF_4$. Abstraction of the chlorine atom bound to the palladium was key to generating the vacant site to allow the second palladium halide moiety approach, resulting in the chlorine-bridged dinuclear complexes.

Experimental Section

General Procedures. All manipulations involving air- and moisture-sensitive organometallic compounds were carried out by using the standard Schlenk techniques under an argon atmosphere. Hexane, THF, toluene, and diethyl ether were dried over sodium benzophenone ketyl and then distilled prior to use. Ethanol and methanol were distilled from magnesium alkoxide. Dehydrated dichloromethane and acetonitrile were purchased from Wako Chemical and degassed. Palladium and nickel complexes, $PdCl_2(PhCN)_2$,[39] PdMeCl(cod),[40] and $NiClPh(PPh_3)_2$,[41] were prepared following the literature procedures. 4-Methyl-2,6-di(2,6-diisopropylphenyliminomethyl)phenol (**1a**) was prepared according to the literature procedure.[31] Syntheses of 4-methyl-2,6-di(2,4,6-tri-*tert*-butylphenyliminometyl)phenol (**1b**) and 3,6-bis(imino(2,6-diisopropylphenyl))pyridazine (**2**) are given in the Supporting Information. Other chemicals were purchased and used as received.

Nuclear magnetic resonance [^{1}H (300 MHz), ^{13}C (75 MHz)] spectra were measured on a Varian Mercury300-C/H. Mass spectra were measured on a JEOL JMS-700 mass spectrometer. Other spectra were recorded by the use of the following instruments: IR, Jasco FT/IR-230 and FT/IR-410; UV/vis spectra, Hewlett Packard HP 8453. Elemental analyses were performed on a Perkin-Elmer 2400 microanalyzer at the Faculty of Engineering Science, Osaka University. All melting points were recorded on a Yanaco MP-52982 and were not corrected.

Preparation of Dinuclear Complex 4a. A solution of 4-methyl-2,6-di(2,6-diisopropylphenyliminometyl)phenol (**1a**) (2.01 g, 4.16 mmol) in THF (20 mL) was added into sodium hydride (104 mg, 4.31 mmol; 1 equiv relative to **1a**) placed in an 80 mL Schlenk tube. After the reaction mixture was stirred at room temperature for 1 h, all volatiles were removed under reduced pressure to give **3a** (134 mg, 267 μmol), which was dissolved in toluene (4 mL). A solution of $PdCl_2(PhCN)_2$ (207 mg, 557 μmol, 2 equiv relative to **3a**) in toluene (14 mL) was added. The reaction mixture was stirred at room temperature for 12 h and then was filtered through a pad of Celite eluted with dichloromethane. The resulting solution was concentrated under reduced pressure, and the resulting product was recrystallized from a mixture of dichloromethane and hexane at room temperature to give orange crystals of **4a** (69 mg, 32% yield), mp 297 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$, 35 °C): δ 7.50−7.13 (m, 10H, Ar-*H*, C*H*=N), 3.53 (sept, $^3J_{H-H}$ = 6.9 Hz, 4H, C*H*$(CH_3)_2$), 2.32 (s, 3H, CH_3), 1.48 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH(C*H*$_3)_2$), 1.15 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH(C*H*$_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$, 35 °C): δ 163.0 (d, $^1J_{C-H}$ = 166 Hz, *C*=N), 146.0 (Ar), 145.6 (Ar), 140.8 (Ar), 129.6 (Ar), 129.0 (d, $^1J_{C-H}$ = 161 Hz, Ar), 128.3 (Ar), 123.5 (Ar), 119.3 (Ar), 29.0 (d, $^1J_{C-H}$ = 127 Hz, *C*H$(CH_3)_2$), 24.7 (q, $^1J_{C-H}$ = 121 Hz, CH(C*H*$_3)_2$), 23.1 (q, $^1J_{C-H}$ = 121 Hz, CH(C*H*$_3)_2$), 19.6 (Ar-*C*H_3). IR (KBr ν in cm^{-1}): 1623 (C=N). UV/vis [CH_2Cl_2, λ in nm (ϵ in cm^{-1} M^{-1})]: 412 (4.0×10^3). MS (FAB): *m*/*z* 800 (M^+). Anal. Calcd for $C_{33}H_{41}Cl_3N_2OPd_2(CH_2Cl_2)_{0.5}$: C, 47.71; H, 5.02; N, 3.32. Found: C, 47.87; H, 5.09; N, 3.28.

Preparation of Dinulcer Complex 4b. To the sodium compound **3b** (205 mg, 304 μmol) in toluene (5 mL) was added a solution of $PdCl_2(PhCN)_2$ (247 mg, 643 μmol) in toluene (5 mL) at room temperature. After the mixture was stirred for 12 h, the reaction solution was filtered through a Celite pad eluted with dichloromethane. The solvent was concentrated under reduced pressure, and the resulting product was recrystallized from a mixture of dichloromethane and hexane at room temperature to give orange crystals of **4b** (236 mg, 80% yield), mp 244 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$, 35 °C): δ 7.60−7.18 (m, 6H, Ar), 7.50 (s, 2H, C*H*=N), 2.23 (s, 3H, CH_3), 1.69 (s, 36H, C(C*H*$_3)_3$), 1.23 (s, 18H, C(C*H*$_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 35 °C): δ 164.1 (d, $^1J_{C-H}$ = 172 Hz, *C*=N), 148.6 (Ar), 145.5 (Ar), 140.5 (Ar), 132.6 (Ar), 132.1 (Ar), 129.0 (dd, $^1J_{C-H}$ = 154 Hz, $^3J_{C-H}$ = 6 Hz, Ar), 124.4 (d, $^3J_{C-H}$ = 7 Hz, Ar), 118.9 (d, $^3J_{C-H}$ = 8 Hz, Ar), 37.8 (*C*$(CH_3)_3$), 35.1 (*C*$(CH_3)_3$), 32.8 (q, $^1J_{C-H}$ = 126 Hz, C(C*H*$_3)_3$), 31.4 (q, $^1J_{C-H}$ = 126 Hz, C(C*H*$_3)_3$), 19.6 (q, $^1J_{C-H}$ = 127 Hz, Ar-*C*H_3). IR (KBr ν in cm^{-1}): 1620 (C=N). UV/vis [CH_2Cl_2, λ in nm (ϵ in cm^{-1} M^{-1})]: 406 (1.4×10^4). MS (FAB): *m*/*z* 897 ($M^+ - {}^t$Bu − CH_3), 755 ($M^+ - 3{}^t$Bu − $3CH_3$). Anal. Calcd for $C_{45}H_{65}Cl_3N_2OPd_2(H_2O)_{1.5}$: C, 54.25; H, 6.88; N, 2.81. Found: C, 54.63; H, 7.20; N, 3.29.

Detection of *in Situ* Generated 5a. To the sodium compound **3a** (31 mg, 62 μmol) in toluene (3 mL) was added a solution of $PdCl_2(PhCN)_2$ (25 mg, 67 μmol) in toluene (3 mL) at room temperature. After the mixture was stirred for 12 h, toluene was removed under reduced pressure to give **5a** as brown powders, whose NMR could not be observed.

Preparation of Dimer Complex 6a. To the sodium compound **3a** (178 mg, 352 μmol) in acetonitrile (20 mL) was added a solution of $PdCl_2(PhCN)_2$ (135 mg, 351 μmol) in acetonitrile (10 mL) at room temperature. After the mixture was stirred for 12 h, the reaction solution was concentrated under reduced pressure. The residue was washed with hexane to give **6a** as orange powders.

(39) Doyle, J. R.; Slade, P. E.; Jonassen, H. B. *Inorg. Synth.* **1960**, *6*, 218.

(40) Rulke, R. E.; Ernsting, J. M.; Spek, A. L.; Elsevier, C. J.; van Leeuwen, P. W. N. M.; Veieze, K. *Inorg. Chem.* **1993**, *32*, 5769.

(41) Hidai, M.; Kashiwagi, T.; Ikeuchi, T.; Uchida, Y. *J. Organomet. Chem.* **1971**, *30*, 279.

The resulting product was recrystallized from dichloromethane to give orange crystals (185 mg, 150 μmol, 43% yield), mp 284 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 35 °C): δ 10.28 (s, 2H, C*H*═N), 7.43−7.01 (m, 20H, Ar, C*H*═N), 3.48−3.42 (m, 8H, C*H*$(CH_3)_2$), 1.76 (s, 6H, CH_3), 1.40 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.35 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.08 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 0.97 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$, 35 °C): δ 165.0 (d, $^1J_{C-H}$ = 149 Hz, *C*═N), 163.9 (d, $^1J_{C-H}$ = 149 Hz, *C*═N), 163.1, 149.1, 145.2, 141.5, 140.7, 139.1, 139.0, 128.9, 128.1, 126.8, 125.2, 123.6, 123.3, 122.8, 121.7, and 119.0 (Ar), 28.8 (d, $^1J_{C-H}$ = 136 Hz, *C*H(CH$_3$)$_2$), 28.7 (d, $^1J_{C-H}$ = 136 Hz, *C*H(CH$_3$)$_2$), 24.6 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 23.7 (CH(*C*H$_3$)$_2$), 22.9 (CH(*C*H$_3$)$_2$), 19.8 (*C*H$_3$). IR (KBr ν in cm^{-1}): 1635 (C═N), 1617 (C═N). UV/vis [CH_2Cl_2, λ in nm (ϵ in cm^{-1} M^{-1})]: 431 (1.1 × 10^4). MS (FAB): *m*/*z* 1211(M$^+$ − Cl), 1068 (M$^+$ − 3CH(CH$_3$)$_2$ − Me − Cl + 1). Anal. Calcd for $C_{66}H_{82}Cl_2N_4O_2Pd_2(C_6H_{14})_{1.4}$: C, 65.33; H, 7.49; N, 4.10. Found: C, 65.82; H, 7.77; N, 4.59.

Preparation of Dimethyl Dinuclear Complex 7a. To a solution of **3a** (134 mg, 267 μmol) in toluene (4 mL) at room temperature was added a solution of (cod)PdMeCl (207 mg, 557 μmol) in toluene (14 mL). The reaction mixture was stirred at room temperature for 12 h, and then toluene was removed under reduced pressure. The residue was washed with hexane to give **6a** as a yellow powder in quantitative yield, mp 169 °C (dec). ^{1}H NMR (300 MHz, C_6D_6, 35 °C): δ 7.60 (s, 2H, C*H*═N), 7.20−7.04 (m, 6H, Ar), 6.62 (s, 2H, Ar), 3.60 (qq, $^3J_{H-H}$ = 6.9 Hz, 4H, C*H*$(CH_3)_2$), 1.83 (s, 3H, C*H*$_3$), 1.24 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.00 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 0.67 (s, 6H, PdC*H*$_3$). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.86 (s, 2H, C*H*═N), 7.26−7.17 (m, 8H, Ar), 3.60 (qq, $^3J_{H-H}$ = 6.9 Hz, 4H, C*H*$(CH_3)_2$), 2.23 (s, 3H, C*H*$_3$), 1.33 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 1.11 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH(C*H*$_3$)$_2$), 0.12 (s, 6H, PdC*H*$_3$). ^{13}C NMR (75 MHz, C_6D_6, 35 °C): δ 166.8 (*C*═N), 148.9 (Ar), 145.2 (Ar), 141.7 (Ar), 128.5 (Ar), 125.7 (Ar), 126.9 (Ar), 124.7 (Ar), 123.3 (Ar), 29.5 (*C*H(CH$_3$)$_2$), 26.2 (CH(*C*H$_3$)$_2$), 24.0 (CH(*C*H$_3$)$_2$), 20.7 (*C*H$_3$), −0.9 (PdC*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 165.3 (d, $^1J_{C-H}$ = 164 Hz, *C*═N), 146.8 (Ar), 144.0 (d, $^1J_{C-H}$ = 153 Hz, Ar), 140.0 (Ar), 126.4 (Ar), 124.4 (Ar), 123.7 (Ar), 123.3 (Ar), 121.3 (Ar), 27.9 (d, $^1J_{C-H}$ = 128 Hz, *C*H(CH$_3$)$_2$), 25.1 (q, $^1J_{C-H}$ = 127 Hz, CH(*C*H$_3$)$_2$), 22.9 (q, $^1J_{C-H}$ = 127 Hz, CH(*C*H$_3$)$_2$), 19.9 (q, $^1J_{C-H}$ = 127 Hz, *C*H$_3$), −2.1 (q, $^1J_{C-H}$ = 127 Hz, Pd*C*H$_3$). IR (KBr ν in cm^{-1}): 1617 (C═N). UV/vis [CH_2Cl_2, λ in nm (ϵ in cm^{-1} M^{-1})]: 456 (6.1 × 10^3). MS (FAB): *m*/*z* 729 (M$^+$ − 2CH$_3$), 686 (M$^+$ − 2CH$_3$ − CH(CH$_3$)$_2$). Anal. Calcd for $C_{35}H_{47}ClN_2OPd_2(C_6H_{14})_{1.0}$: C, 47.71; H, 5.02; N, 3.32. Found: C, 47.87; H, 5.09; N, 3.28.

Preparation of Dimethyl Dinuclear Complex 7b. To a solution of **3b** (134 mg, 267 μmol) in toluene (4 mL) at room temperature was added a solution of (cod)PdMeCl (207 mg, 557 μmol) in toluene (14 mL). The reaction mixture was stirred at room temperature for 12 h, and then toluene was removed under reduced pressure. The residue was washed with hexane to give **7b** as a yellow powder in quantitative yield, mp 172 °C (dec). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 7.86 (s, 2H, C*H*═N), 7.58 (s, 4H, Ar), 6.73 (s, 2H, Ar), 1.86 (s, 3H, C*H*$_3$), 1.71 (s, 36H, C(C*H*$_3$)$_3$), 1.31 (s, 18H, C(C*H*$_3$)$_3$), 0.84 (s, 6H, PdC*H*$_3$). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): 166.9 (d, $^1J_{C-H}$ = 164 Hz, *C*═N), 159.8, 147.7, 147.1, 143.8, 139.9, 128.3, 124.1 (dd, $^1J_{C-H}$ = 154 Hz, $^3J_{C-H}$ = 7 Hz) and 121.0 (Ar), 37.7 (*C*(CH$_3$)$_3$), 36.0 (*C*(CH$_3$)$_3$), 31.8 (d, $^1J_{C-H}$ = 126 Hz, C(*C*H$_3$)$_3$), 31.4 (d, $^1J_{C-H}$ = 126 Hz, C(*C*H$_3$)$_3$), 19.8 (*C*H$_3$), −1.2 (q, $^1J_{C-H}$ = 135 Hz, Pd-CH$_3$). IR (KBr ν in cm^{-1}): 1619 (C═N). UV/vis [CH_2Cl_2, λ in nm (ϵ in cm^{-1} M^{-1})]: 452 (1.0 × 10^4). MS (EI$^+$): *m*/*z* 913 (M$^+$ − CH$_3$), 897 (M$^+$ − 2CH$_3$ − H). Anal. Calcd for $C_{47}H_{71}ClN_2OPd_2(C_6H_5CH_3)_{1.8}$: C, 65.42; H, 7.87; N, 2.56. Found: C, 65.04; H, 8.37; N, 2.56.

Preparation of Nickel Complex 8. To a solution of **3a** (453 mg, 902 μmol) in toluene (10 mL) at room temperature was added a solution of $NiClPh(PPh_3)_2$ (1.34 g, 1.90 mmol) in toluene (15 mL). The reaction mixture was stirred at room temperature for 12 h, and then toluene was removed under reduced pressure to give green powders. The resulting product was recrystallized from hexane to give green crystals (451 mg, 441 μmol, 98% yield), mp 251 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$, 35 °C): δ 7.96 (s, 1H, C*H*═N), 7.27−7.09 (m, 12H, Ar, C*H*═N), 6.85 (s, 1H, Ar), 6.62 (d, $^3J_{H-H}$ = 7.7 Hz, 2H, Ar), 5.83−5.75 (m, 2H, Ar), 4.31 (sept, $^3J_{H-H}$ = 6.6 Hz, 2H, C*H*$(CH_3)_2$), 2.60 (sept, $^3J_{H-H}$ = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 2.18 (s, 3H, C*H*$_3$), 1.43 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.32 (d, $^3J_{H-H}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.19 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.00 (d, $^3J_{H-H}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR (75 MHz, $CDCl_3$, 35 °C): δ 165.4 (d, $^1J_{C-H}$ = 157 Hz, *C*═N), 160.7 (Ar), 156.2 (d, $^1J_{C-H}$ = 170 Hz, *C*═N), 150.3 (Ar), 145.8 (Ar), 140.9 (Ar), 136.4 (Ar), 146.2 (Ar), 134.1 (Ar), 128.9 (Ar), 128.1 (Ar), 126.5 (d, $^1J_{C-H}$ = 161 Hz, Ar), 126.4 (Ar), 124.1 (Ar), 123.5 (Ar), 122.7 (Ar), 121.8 (Ar), 120.8 (Ar), 29.1 (d, $^1J_{C-H}$ = 127 Hz, *C*H(CH$_3$)$_2$), 27.9 (d, $^1J_{C-H}$ = 127 Hz, *C*H(CH$_3$)$_2$), 23.9 (q, $^1J_{C-H}$ = 125 Hz, CH(*C*H$_3$)$_2$), 23.7 (q, $^1J_{C-H}$ = 125 Hz, CH(*C*H$_3$)$_2$), 23.5 (q, $^1J_{C-H}$ = 125 Hz, CH(*C*H$_3$)$_2$), 22.4 (q, $^1J_{C-H}$ = 125 Hz, CH(*C*H$_3$)$_2$), 19.9 (q, $^1J_{C-H}$ = 127 Hz, *C*H$_3$). IR (KBr ν in cm^{-1}): 1622 (C═N), 1598 (C═N). UV/vis [CH_2Cl_2, λ in nm (ϵ in cm^{-1} M^{-1})]: 469 (1.2 × 10^4), 354 (1.8 × 10^4). MS (FAB): *m*/*z* 1021 (M$^+$ − H), 979 (M$^+$ − H − CH(CH$_3$)$_2$), 834 (M$^+$ − CH$_3$ − 3CH(CH$_3$)$_2$). We could not obtain a satisfactory elemental analysis due to the contamination of triphenylphosphine oxide.

Preparation of Dinuclear Complex 9a. A solution of $AgBF_4$ (129.8 mg, 0.67 mmol) and CH_3CN (15 mL) was added to a solution of **2** (300.0 mg, 0.66 mmol) and $(PhCN)_2PdCl_2$ (506.2 mg, 1.32 mmol) in CH_3CN (15 mL). The reaction mixture was stirred for 12 h at room temperature. The mixture was extracted with CH_3CN and then filtered to remove AgCl. After evaporation of the solvent, the orange solid was washed with Et_2O. The orange solid was dried under reduced pressure to give **9a** (550.2 mg, 0.64 mmol, 97%), mp 215−219 °C (dec).

Stepwise synthesis was alternatively conducted. A solution of $AgBF_4$ (108.1 mg, 0.55 mmol) in CH_3CN (5 mL) was added to a solution of complex **10** (319.0 mg, 0.50 mmol) in CH_3CN (10 mL). The reaction mixture was stirred for 30 min at room temperature. After a solution of $(PhCN)_2PdCl_2$ (193.6 mg, 0.50 mmol) in CH_3CN (10 mL) was added to the resulting red solution, the reaction mixture was further stirred for 12 h. The filtration was conducted to remove AgCl. After evaporation of all volatiles, the orange solid was washed with Et_2O and then dried under reduced pressure, yielding **9a** in 96% yield. ^{1}H NMR (300 MHz, CD_2Cl_2, 30 °C): δ 9.30 (s, 2H, pyridazine), 8.68 (s, 2H, C*H*═N), 7.22−7.24 (m, 6H, Ar), 3.18 (qq, $^3J_{H-H}$ = 6.7 Hz, 4H, C*H*$(CH_3)_2$), 1.36 (d, $^3J_{H-H}$ = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.15 (d, $^3J_{H-H}$ = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$). ^{13}C NMR (75 MHz, CD_2Cl_2, 30 °C): δ 140.4 (*C*H═N), 134.9 (N═*C*-CH of pyridazine), 132.9 (Ar), 129.1 (Ar), 123.4 (N═C-*C*H of pyridazine), 118.3 (Ar), 112.0 (Ar), 29.0 (*C*H(CH$_3$)$_2$), 23.6 (CH(*C*H$_3$)$_2$). UV/vis [CH_2Cl_2, λ in nm (ϵ in cm^{-1} M^{-1})]: 238 (3.6 × 10^4), 354 nm (1.7 × 10^4 dm^3 mol^{-1} cm^{-1}). IR (KBr ν in cm^{-1}): 1083 (B−F), 1652 (C═N). Anal. Calcd for $C_{30}H_{38}N_4$: C, 41.87; H, 4.45; N, 6.51. Found: C, 41.99; H, 4.92; N, 6.50.

Preparation of Mononuclear Complex 10. A solution of $(PhCN)_2PdCl_2$ (337.5 mg, 0.88 mmol) in CH_3CN (10 mL) was added to a solution of **2** (400.0 mg, 0.88 mmol) in CH_3CN (15 mL). The reaction mixture was stirred for 12 h at room temperature. After removal of all volatiles, the resulting orange solid was washed with Et_2O and then dried under reduced pressure to give **10** (467.8 mg, 0.74 mmol, 84%), mp 294−297 °C (dec). ^{1}H NMR (300 MHz, CD_2Cl_2, 30 °C): δ 8.96 (d, $^3J_{H-H}$ = 8.5 Hz, 1H, pyridazine), 8.73 (s, 1H, C*H*═N), 8.40 (s, 1H, C*H*═N), 8.37 (d, $^3J_{H-H}$ = 8.5 Hz, 1H, pyridazine), 7.22−7.28 (m, 6H, Ar), 3.27 (sep, $^3J_{H-H}$ = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 2.92 (sept, $^3J_{H-H}$ = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 1.40 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 1.16−1.20 (m, 18H,

$CH(CH_3)_2$). ^{13}C NMR (75 MHz, CD_2Cl_2, 35 °C): δ 166.7, 158.9, 158.8, 158.4, 143.1, 140.8, 137.0, 132.8$_6$, 132.8$_5$, 129.4, 127.6, 126.0, 123.6, 123.5, 29.1 ($CH(CH_3)_2$), 28.3 ($CH(CH_3)_2$), 24.3 ($CH(CH_3)_2$), 23.2 ($CH(CH_3)_2$), 22.9 ($CH(CH_3)_2$). Anal. Calcd for $(C_{30}H_{38}N_4Cl_2Pd_2)(H_2O)$: C, 55.43; H, 6.20; N, 8.62. Found: C, 55.82; H, 5.87; N, 8.70. The presence of solvated water molecule was confirmed by the ^1H NMR.

Preparation of Dimethyl Dinucler Complex 9b. A solution of $AgBF_4$ (272.3 mg, 1.39 mmol, 1.1 equiv) in CH_2Cl_2 (10 mL) was added to a solution of **2** (565.6 mg, 1.24 mmol) and PdClMe(cod) (725.5 mg, 2.73 mmol, 2.2 equiv) in CH_2Cl_2 (20 mL) at −78 °C. After the reaction mixture was slowly warmed to room temperature, it was stirred for 2 h. The reaction mixture was filtered to remove AgCl. Removal of all volatiles gave an orange solid, which was washed with hexane and then dried under reduced pressure, yielding **9b** (99.2 mg, 1.21 mmol, 98%).

Stepwise synthesis was also carried out. A solution of $AgBF_4$ (30.6 mg, 0.16 mmol, 1.2 equiv) in CH_2Cl_2 (5 mL) was added to a solution of the mixture of complexes **12a** and **12b** (76.3 mg, 0.12 mmol) and PdClMe(cod) (33.0 mg, 0.12 mmol) in CH_2Cl_2 (5 mL) at −78 °C. The reaction mixture was slowly warmed to room temperature and then stirred for 2 h. After removal of AgCl by filtration, the solution was concentrated to leave an orange solid, which was washed with hexane and then dried under reduced pressure, giving **9b** (96.4 mg, 0.12 mmol, 98% yield). ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ 9.07 (s, 2H, pyridazine), 8.98 (s, 2H, C*H*═N), 7.20−7.40 (m, 6H, Ar), 3.13 (sep, $^3J_{H-H}$ = 6.9 Hz, 4H, C*H*$(CH_3)_2$), 1.31 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, H CH(C*H*$_3)_2$), 1.18 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH(C*H*$_3)_2$), 0.77 (s, 6H, PdMe). ^{13}C NMR (75 MHz, CD_2Cl_2, 25 °C): δ 167.4 (*C*H═N), 152.8 (N═*C*-CH of pyridazine), 142.2 (Ar), 139.0 (Ar), 134.5 (N═C-*C*H of pyridazine), 128.5 (Ar), 123.4 (Ar), 28.1 (*C*H$(CH_3)_2$), 23.8 (CH(*C*H$_3)_2$), 22.1 (CH(*C*H$_3)_2$), 7.4 (PdMe). UV/vis [CH_2Cl_2, λ in nm (ϵ in cm^{-1} M^{-1})]: λ_{max} (ϵ) = 230 (8.6×10^4), 319 nm (1.7×10^4 dm^3 mol^{-1} cm^{-1}). IR (KBr ν in cm^{-1}): 1059 (B−F), 1634 (C═N). FAB-MS (*m*/*z*): 698 ($M^+ - ClBF_4$), 683 ($M^+ - MeClBF_4$). Anal. Calcd for $C_{32}H_{44}BClF_4N_4Pd_2$: C, 46.88; H, 5.41; N, 6.83. Found: C, 46.94; H, 5.43; N, 6.59.

Preparation of Methyl Mononucler Complexes 12a and 12b. A solution of PdClMe(cod) (105.3 mg, 0.40 mmol) in CH_2Cl_2 (5 mL) was added to a solution of ligand **2** (180.4 mg, 0.40 mmol) in CH_2Cl_2 (5 mL) under argon. The reaction mixture was stirred for 15 h at room temperature. After evaporation of the solution, the orange solid was washed with hexane. The orange solid was dried under reduced pressure, quantitatively giving a mixture of **12a** and **12b**, mp of the mixture 207−210 °C (dec). Major isomer: ^1H NMR(300 MHz, $CDCl_3$, 25 °C): δ 8.79 (s, 1H, C*H*═N), 8.79 (d, $^3J_{H-H}$ = 8.5 Hz, 1H, pyridazine), 8.67 (s, 1H, C*H*═N), 8.32 (d, $^3J_{H-H}$ = 8.5 Hz, 1H, pyridazine), 7.11−7.34 (m, 6H, Ar), 3.22 (sep, $^3J_{H-H}$ = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 2.85 (sep, $^3J_{H-H}$ = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 1.27 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$), 1.14 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH(C*H*$_3)_2$), 1.11 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$), 0.79 (s, 3H, PdMe). Minor isomer: ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 8.85 (d, $^3J_{H-H}$ = 8.5 Hz, 1H, pyridazine), 8.62 (s, 1H, C*H*═N), 8.48 (s, 1H, C*H* = N), 8.32 (d, $^3J_{H-H}$ = 8.5 Hz, 1H, pyridazine), 7.11−7.34 (m, 6H, Ar), 3.18 (sep, $^3J_{H-H}$ = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 2.88 (sep, $^3J_{H-H}$ = 6.9 Hz, 2H, C*H*$(CH_3)_2$), 1.61 (s, 3H, PdMe), 1.31 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$), 1.19 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, CH(C*H*$_3)_2$), 1.18 (d, $^3J_{H-H}$ = 6.9 Hz, 12H, CH(C*H*$_3)_2$). MS (FAB): *m*/*z* 609 ($M^+ - H$). Elemental analysis of the mixture gave a somewhat larger carbon content: Calcd for $C_{31}H_{41}ClN_4Pd$: C, 60.88; H, 6.78; N, 9.16. Found: C, 61.64; H, 7.79; N, 9.12.

X-ray Crystallographic Analyses. All crystals were handled similarly. The crystals were mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 120(1) K. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite-monochromated Mo Kα (0.71075 Å) radiation. The crystal-to-detector distance was 127.40 mm. The data were corrected for Lorentz and polarization effects. Crystal data and structure refinement parameters are summarized in Table S3 (see Supporting Information). The structure was solved by direct methods (SIR92[42] (**7a** and **8**), SIR2002[43] (**4a**), SIR2004[44] (**4b** and **6a**), and SHELXS-97[45] (**9b**)) and refined on F^2 by full-matrix least-squares methods, using SHELXL-97.[45] Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(F_o^2 - F_c^2)^2]$ ($w = 1/[\sigma^2 (F_o^2) + (aP)^2 + bP]$), where $P = (\max(F_o^{2,0}) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The function R_1 and wR_2 were $(\sum||F_o| - |F_c||)/\sum|F_o|$ and $[\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^4)]^{1/2}$, respectively. The ORTEP-3 program[46] was used to draw the molecule.

Supporting Information Available: Tabulations of crystallographic data in CIF format for **4a**, **4b**, **6a**, **7a**, **8**, and **9b**; synthesis and characterization of ligands **1b** and **2**; tables of crystal data and refinement parameters for **4a**, **4b**, **6a**, **7a**, **8**, and **9b**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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