Synthesis and Decomposition Behavior of a C_2-Symmetrical Palladium(IV) Spirocyclic Complex

Yoshihiko Yamamoto,*,† Shoji Kuwabara,† Shigeo Matsuo,‡ Takuya Ohno,‡ Hisao Nishiyama,† and Kenji Itoh‡

Department of Applied Chemistry and Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Chikusa, Nagoya 464-8603, Japan

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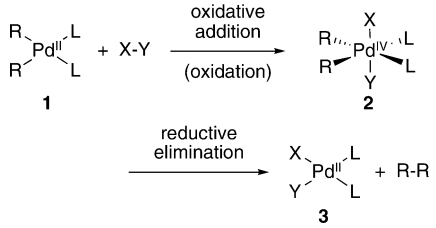
A novel palladium(IV) complex consisting of a C_2-symmetrical palladaspirocycle framework and an ether ligand was assembled only in a single step from commercially available $Pd_2(dba)_3$, tetrachloro-1,2-benzoquinone (*o*-chloranil), and norbornene. The solid-state structure was confirmed by X-ray analysis of a THF complex. The ligand exchange from diethyl ether to pyridine converted the trigonal-bipyramidal complex to a distorted-octahedral bis(pyridine) complex. Similar palladium(IV) spirocyclic complexes were also formed from the reaction of $Pd_2(dba)_3$ with *o*-chloranil and benzonorbornadiene. The benzonorbornadiene-derived complexes exhibited pronounced stability in both the solid state and solution. The complete decomposition of the mono(pyridine) complex required several hours in C_6D_6 at 70 °C, and the addition of extra pyridine retarded the decomposition rate. Benzonorbornadiene was obtained as the main organic product, together with two isomeric adducts between *o*-chloranil and benzonorbornadiene. On the other hand, the decomposition of the pyridine complex took place within 15 min even at −40 to −50 °C, upon exposure to HCl in a $CDCl_3$ solution.

Introduction

Palladium is an extensively studied transition-metal element in organometallic chemistry as a versatile promoter of various stoichiometric and catalytic organic transformations.[1] Although palladium generally prefers low oxidation states from 0 to +2, the involvement of organopalladium(IV) intermediates has been invoked in significant catalytic processes.[2] In contrast to platinum, which has an extensive organometallic chemistry in the +4 oxidation state,[3] organopalladium(IV) complexes had hardly been studied until the first unequivocal trialkylpalladium(IV) complex, $PdIMe_3(bpy)$ (bpy = 2,2′-bipyridine), was isolated and characterized by X-ray analysis.[4] Since this report, various alkylpalladium(IV) complexes **2** were synthesized from palladium(II) precursors **1** possessing a nitrogen ligand (L_2 = 2,2′-bipyridine, 1,10-phenanthroline, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, etc.) by oxidative addition of alkyl halides or by oxidation with H_2O, halogens, dichalcogenides, etc.[5] Most of them are thermally labile, with the reductive elimination of an organic molecule readily occurring at or below room temperature to give rise to the corresponding palladium(II) fragments **3** (Scheme 1).[6] In striking contrast, we recently communicated that the reaction of a readily available palladium(0) complex, $Pd_2(dba)_3$ (dba = dibenzilideneacetone), with tetrachloro-1,2-benzoquinone (*o*-chloranil) and norbornene directly produced the novel C_2-symmetrical palladium(IV) spirocycle complex **4** in high yield (Scheme 2).[7] The obtained Pd(IV) complex is stable in the solid state as well as in a THF-d_8 solution, but it decomposed in $CDCl_3$. In

Scheme 1



* To whom correspondence should be addressed. E-mail: yamamoto@apchem.nagoya-u.ac.jp.
† Department of Applied Chemistry.
‡ Department of Molecular Design and Engineering.

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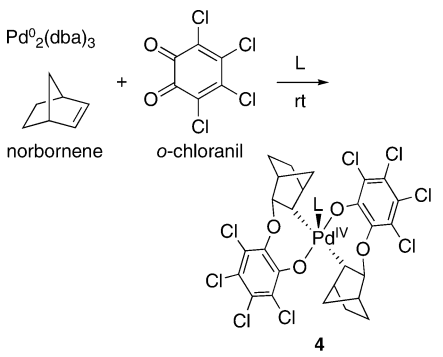
Scheme 2



further screening of the bicycloalkene components, we found that benzonorbornene affords similar palladaspirocyclic complexes, which have a greater stability in both the solid state and in solution. In this Article, we report the synthesis and decomposition behavior of the C_2-symmetrical palladium(IV) spirocyclic complexes.

Results and Discussion

Formation of Palladium(IV) Spirocyclic Complexes with $Pd_2(dba)_3$, *o*-Chloranil, and Norbornene. Quinones have received considerable attention in coordination chemistry as redox-active, electron-accepting ligands. In contrast to *p*-quinones, which are coordinated by various transition metals at their localized ring olefinic bonds,[8] *o*-quinones usually form complexes containing semiquinone or hydroquinone chelate ligands with the concomitant oxidation of transition-metal centers.[9] For instance, the reaction of the Pd(0)−phosphine complex $Pd(PPh_3)_4$ with *o*-chloranil has been reported to furnish the palladium(II) tetrachlorocatecholate complex $(Ph_3P)_2Pd(O_2C_6Cl_4)$.[10] In striking contrast, the treatment of the Pd(0) olefin complex $Pd_2(dba)_3$ with 5 equiv each of *o*-chloranil and norbornene at ambient temperature in acetone for 30 min followed by addition of diethyl ether gave rise to the novel palladium(IV) spirocyclic complex **4a** (L = OEt_2) in 81% yield (Scheme 2). The absence of the intact *o*-quinone ring was confirmed by its IR spectrum, which showed no C=O absorption. The ^{1}H NMR (300 MHz, $CDCl_3$) spectrum showed signals at δ 1.0−5.0 ppm, which were assigned to norbornyl moieties and coordinated diethyl ether. The ether complex **4a** is readily soluble in acetone, THF, and $CHCl_3$, but it slowly decomposed to deposit black materials in $CHCl_3$. Upon treatment with THF at ambient temperature, **4a** was quantitatively converted to the THF complex **4b** (L = THF). To obtain further structural information, we characterized **4b**, which is stable in degassed THF at ambient temperature. The ^{13}C NMR (125 MHz, THF-d_8) spectrum of **4b** showed four signals (δ 117.84, 122.49, 124.87, and 128.20 ppm) that were assigned to the aromatic C−Cl carbon atoms, and two lower-field signals (δ 144.76 and 157.24 ppm) were assigned to the aromatic C−O carbons. These observations are indicative of an unsymmetrical tetrachlorocatecholate ring being present in **4b**. In addition, seven signals observed at higher field (δ 24−100 ppm) are assigned to norbornane rings in an unsymmetrical environment. The structure of **4b** was unambiguously confirmed by a single-crystal X-ray diffraction study. As shown in Figure 1, **4b** is a dialkylpalladium(IV) complex with a trigonal-bipyramidal geometry. Two molecules each of *o*-chloranil and norbornene were coupled on the palladium center to form a pair of unprecedented seven-membered chelete rings. Their O and C termini occupy the axial and equatorial positions, respectively. The third equatorial position accommodates a THF molecule. The Pd1−O1 and Pd1−O3 bonds of 2.0004(13) and 2.0012(13) Å, respectively, are slightly shorter than those in the known Pd(II) tetrachlorocatecholate complex (2.028(5) and 2.039(5) Å), which are elongated by the trans influence of PPh_3 ligands.[11] The four C−O bonds in the catecholate moieties at 1.320−1.378 Å are close to that expected for a C(sp^2)−O single bond (1.34 Å).[12] The C(sp^2)−C(sp^2)

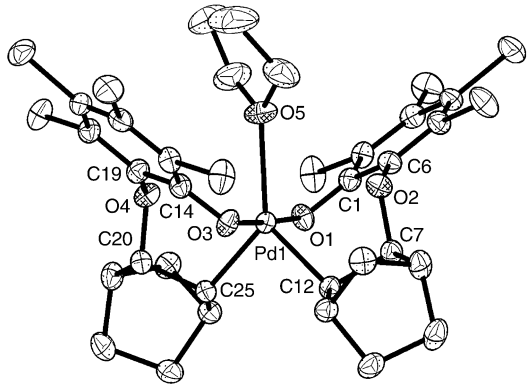


Figure 1. ORTEP diagram of **4b**. All hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (deg): Pd1−O1, 2.0012(13); Pd1−O3, 2.0004(13); Pd1−C12, 2.0361(17); Pd1−C25, 2.0405(17); Pd1−O5, 2.3751(14); O1−C1, 1.321(2); O3−C14, 1.320(2); O2−C6, 1.377(2); O4−C19, 1.378(2); O2−C7, 1.463(2); O4−C20, 1.462(2); O1−Pd1−O3, 177.02(5); C12−Pd1−C25, 88.98(7); O5−Pd1−C12, 136.36(6); O5−Pd1−C25, 134.67(6).

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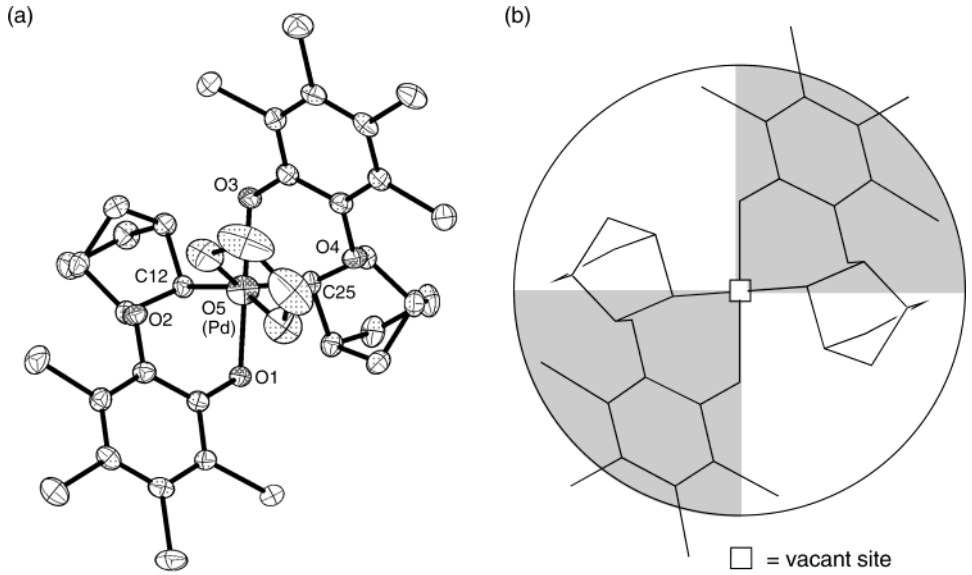

Figure 2. (a) ORTEP diagram of **4b** projected down the O5−Pd axis and (b) schematic representation of the palladaspirocyclic framework.

bonds within the benzene rings (1.390(3)−1.407(2) Å) show no evidence of residual benzoquinone character. The Pd−C bonds of 2.0361(17) and 2.0405(17) Å are similar to those of Pd^{IV}−Me bonds in the previous examples.[5] All isolated examples of polyalkylpalladium(IV) complexes to date are confined to octahedral complexes containing bidentate or tripodal donor supporting ligands, which prevent the formation of the five-coordinate intermediates that are required for facile reductive elimination of an alkane. On the other hand, the trigonal-bipyramidal complexes **4** are stable in the solid state without any bidentate or tripodal spectator donor ligands. The complete decomposition of **4b** in degassed THF requires several days at ambient temperature. This observation is also in contrast to the fact that relevant dialkylpalladium(IV) complexes possessing Pd−O_2CAr bonds are unstable at or below 20 °C, even though they have tris(pyrazol-1-yl)borate or 2,2′-bipyridyl ligands.[13] The remarkable stability of **4** can be ascribed to the formation of a chelate ring connecting the labile tetrachlorocatecholate and norbornyl rings.

Figure 2a shows the ORTEP diagram of **4b** projected down the O5−Pd1 axis. Interestingly, the palladaspirocyclic framework has C_2 symmetry, and this is illustrated by the schematic representation in Figure 2b. The sterically demanding tetrachlorophenyl rings occupy the gray quadrants, and as a result, the THF molecule occupies the vacant site in such a way that it is placed along the less hindered colorless quadrants. Such a coordination mode is frequently involved in the enantioface differentiation of C_2-chiral asymmetric catalysis.[14]

The palladaspirocycle fragment is a potential C_2-symmetrical Lewis acid receptor bearing the electron-deficient palladium(IV) center. The ligand L in **4** can be replaced by other Lewis basic molecules. In fact, the diethyl ether complex **4a** was dissolved in dry degassed pyridine at ambient temperature to form a new complex **5**. Figure 3 gives its ORTEP diagram. To our surprise, **5** is a *cis*-bis(pyridine) complex having a distorted-octahedral geometry with an O1−Pd1−O2 angle of 165.32(5)°. Two pyridine ligands are incorporated in the equatorial positions. It is interesting to note that the two tetrachlorophenyl rings are turned away from the coordination sites in the same direction as the norbornyl rings. Therefore, the palladaspirocyclic framework has a considerable flexibility to adjust the coordination space to the nature of the coordinated molecules. The coordi-

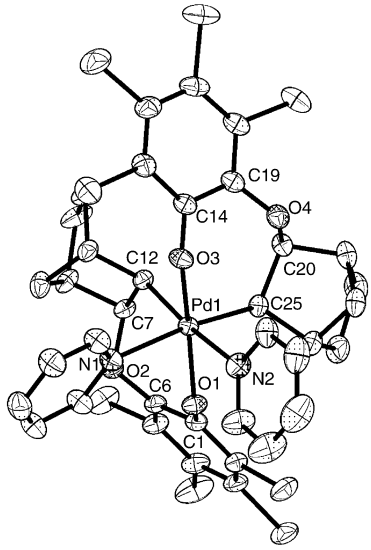

Figure 3. ORTEP diagram of **5**. All hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (deg): Pd1−O1, 2.0248(11); Pd1−O3, 2.0301(11); Pd1−C12, 2.0753(15); Pd1−C25, 2.0741(15); Pd1−N1, 2.2480(14); Pd1−N2, 2.2391(15); O1−C1, 1.3133(19); O3−C14, 1.312(2); O2−C6, 1.3630(18); O4−C19, 1.356(2); O2−C7, 1.4475(18); O4−C20, 1.453(2); O1−Pd1−O3, 165.32(5); C12−Pd1−C25, 84.51(6); N1−Pd1−N2, 85.46(5); N1−Pd1−C12, 95.54(6); N2−Pd1−C25, 95.59(6).

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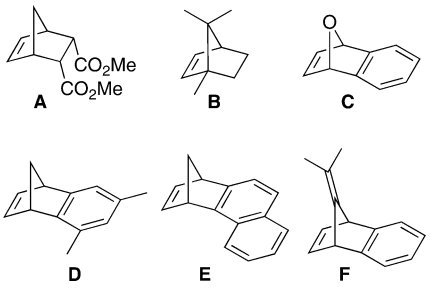
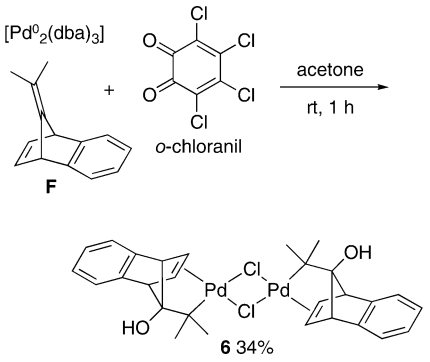
Chart 1. Norbornene and Benzonorbornadiene Derivatives Which Failed To Afford a Palladium(IV) Spirocyclic Complex



Scheme 3



nation number seems to vary depending on the electron-donating ability of the Lewis basic molecules; that is, it increased from 5 for the weaker ether ligands to 6 for the stronger pyridine ligand. In accordance with this observation, the Pd1−C12 and Pd1−C25 bonds in **5** are longer than those in **4b** by 0.0392 and 0.0336 Å, respectively, as a result of the trans influence of the stronger electron donor pyridine.

Reaction of $Pd_2(dba)_3$ with other *o*-Quinones and Olefins. It is noteworthy that the palladaspirocyclic framework was possibly assembled through a tandem oxidative cyclization between *o*-chloranil and norbornene on the palladium(0) center. The formation of both the Pd−C and O−C bonds selectively occurred at the less hindered exo face of norbornene. The combination of *o*-chloranil and norbornene is quite essential for this process. Employing 3,5-di-*tert*-butylbenzoquinone or 9,10-phenanthrenequinone in place of *o*-chloranil failed to give the corresponding palladaspirocycles. In addition, no product was obtained when less strained cyclopentene was used as an olefin component. These results show that both the strong oxidizing ability of *o*-chloranil and the ring strain of norbornene play critical roles in the oxidative cyclization. In this context, a variety of norbornene analogues were further examined as an bicycloalkene component (Chart 1). Whereas benzonorbornadiene turned out to give a similar result with norbornene (see below), other derivatives, including ester-substituted **A**, chiral analogue **B** derived from (+)-camphor, oxabenzonorbornadiene **C**, and benzonorbornadiene derivatives **D** and **E** failed to afford the desired palladaspirocycles. When **F** possessing an isopropylidene bridge was employed, the palladium(II) complex **6** was obtained in 34% yield as colorless solids (Scheme 3). An X-ray diffraction study disclosed that **6** is a dimeric complex with two bridging chloride ligands (Figure 4). The (*β*-hydroxyalkyl)palladium(II) chloride

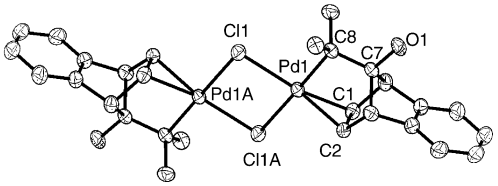
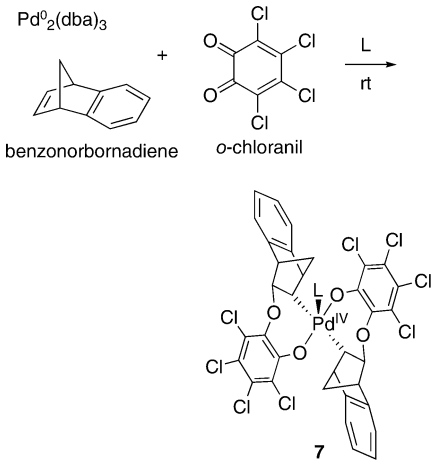


Figure 4. ORTEP diagram of **6**. All hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (deg): Pd−C1, 2.1460(18); Pd−C2, 2.1464(18); Pd−C8, 2.0275(16); Pd−Cl1, 2.5216(5); Pd−Cl1A, 2.5216(5); C1−C2, 1.390(3); C7−C8, 1.526(2); C7−O1, 1.420(2); Cl1−Pd1−Cl1A, 85.820(16); Pd1−Cl1−Pd1A, 94.180(16); Pd1−C1−C2, 71.12(11); Pd1−C2−C3, 71.09(11); C1−Pd1−C2, 37.78(7); Pd1−C8−C7, 103.38(11).

Scheme 4



fragment was probably formed via the trans addition of H_2O to the isopropylidene bridge coordinated by $PdCl_2$,[15] which was initially formed from $Pd_2(dba)_3$ and *o*-chloranil.

Synthesis of a Palladium(IV) Spirocyclic Complex with Benzonorbornadiene. In a similar manner with **4**, the treatment of $Pd_2(dba)_3$ with 10 equiv each of *o*-chloranil and benzonorbornadiene at ambient temperature in acetone for 30 min gave rise to orange precipitates. Upon filtration, the acetone complex **7a** (L = acetone) was obtained in 57% yield (Scheme 4). Its ^{1}H NMR spectrum showed the norbornyl ring protons in an unsymmetrical environment along with the aromatic protons. A detailed structure characterization was carried out with the corresponding THF complex **7b**. The same reaction was performed in THF to give a homogeneous red solution. After dilution with pentane, the concentrated THF solution was allowed to stand overnight at −15 °C to afford **7b** in 78% yield as red crystals. The X-ray analysis unambiguously revealed that **7b** is a palladaspirocyclic complex having a THF molecule at the equatorial position (Figure 5). Its structural parameters are almost the same with those of **4b**, except for the fused benzene rings. The corresponding pyridine complex **7c** (L = pyridine) was also obtained in 78% yield from **7a** upon treatment with 1 equiv of pyridine in $CHCl_3$ at ambient temperature for 1 h. As shown in Figure 6, **7c** is a mono(pyridine) complex having a trigonal-bipyramidal geometry very similar to the THF complex **7b**, rather than the bis-

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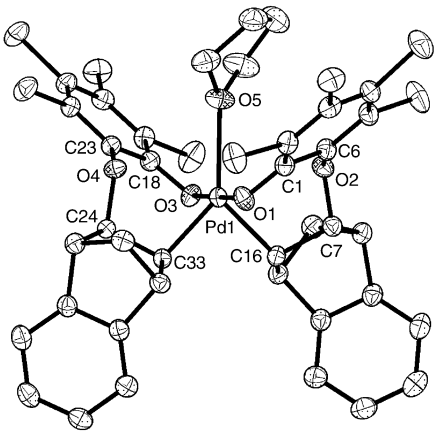

Figure 5. ORTEP diagram of **7b**. All hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (deg): Pd1−O1, 2.0000(15); Pd1−O3, 2.0017(14); Pd1−C16, 2.036(2); Pd1−C33, 2.028(2); Pd1−O5, 2.3771(17); O1−C1, 1.316(2); O3−C18, 1.322(2); O2−C6, 1.376(2); O4−C23, 1.379(2); O2−C7, 1.456(3); O4−C24, 1.467(2); O1−Pd1−O3, 178.82(6); C16−Pd1−C33, 88.91(8); O5−Pd1−C16, 132.93(7); O5−Pd1−C33, 138.03(7).

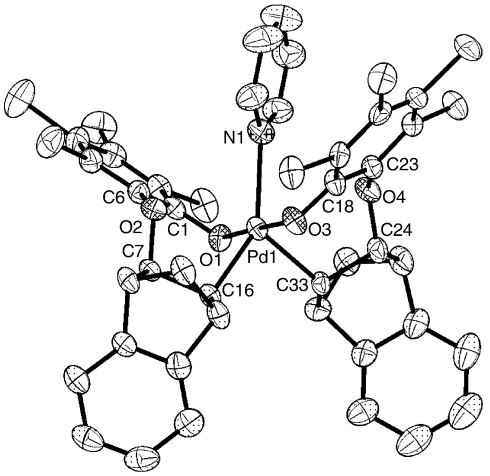

Figure 6. ORTEP diagram of **7c**. All hydrogen atoms were omitted for clarity. Selected bond distances (Å) and angles (deg): Pd1−O1, 2.006(3); Pd1−O3, 2.004(2); Pd1−C16, 2.039(4); Pd1−C33, 2.048(4); Pd1−N1, 2.335(3); O1−C1, 1.312(5); O3−C18, 1.328(4); O2−C6, 1.389(4); O4−C23, 1.379(4); O2−C7, 1.472(4); O4−C24, 1.440(5); O1−Pd1−O3, 178.75(12); C16−Pd1−C33, 87.95(16); N1−Pd1−C16, 147.38(15); N1−Pd1−C33, 124.54(14).

(pyridine) complex **5**. The Pd−N bond distance of 2.335(3) Å is slightly longer than those in **5** (2.2480(14) and 2.2391(15) Å).

It is noteworthy that the fused benzene rings on the norbornyl moieties play some role in the stabilization of the palladaspirocyclic framework. The benzonorbornadiene-derived complexes **7** exhibited pronounced stability even in $CHCl_3$ solutions at ambient temperature. Remarkably, the acetone complex **7a** was chromatographed on silica gel with $CHCl_3$ as an eluent to afford an acetone-free complex as a reddish brown powder. Its ^{1}H NMR spectrum is, however, almost the same as that of **7b**, except for the absorption of THF (part b vs part c in Figure 7). The chemical shifts of THF are also identical in the ^{1}H NMR spectra of **7b** and pure THF (part a vs part c in Figure 7). These data suggest that Lewis basic guests such as acetone and THF readily dissociate in the $CDCl_3$ solutions to produce a four-coordinate species. On the other hand, some peaks of the palladaspirocycle moved upfield in the ^{1}H NMR spectrum of **7c** (part e, Figure 7). Similarly, the upfield shift of the pyridine protons was observed, indicative of it being coordinated by the palladium(IV) center even in the $CDCl_3$ solution.

Thermal and Acid-Promoted Decomposition of Palladaspirocyclic Complexes. Most of the previous octahedral polyalkylpalladium(IV) complexes have been reported to decompose at or below ambient temperature with the concomitant reductive elimination of an alkane through five-coordinate intermediates.[5,6] In striking contrast, it was found that the trigonal-bipyramidal complexes **7** have much greater stability at ambient temperature, even though they are converted to the four-coordinate species in solution via extrusion of the Lewis basic ligands. To obtain further insight into their decomposition behavior, we examined the thermolysis of **7c** (Scheme 5). The 0.005 M solution of **7c** in C_6D_6 was heated to 70 °C. After heating for 4 h, ^{1}H NMR spectroscopy showed that **7c** totally disappeared and instead, benzonorbornadiene **(**bnd**)** was formed in 43% yield together with a trace amount of *trans*-$PdCl_2(py)_2$,[16] which was presumably produced by the reaction of palladium(0) species with *o*-chloranil. In addition, the two organic products **8** and **9** were isolated in 12 and 4% respective yields by silica gel chromatography. The structures of these products were later confirmed by X-ray diffraction studies (Figure 8).

The decomposition of **7c** turned out to be retarded by the pyridine additive. In the presence of 5 equiv of extra pyridine, the complete consumption of **7c** required 50 h at 70 °C. In this case, the palladium(II) fragment was effectively trapped by excess pyridine to afford *trans*-$PdCl_2(py)_2$ in 47% isolated yield. The yields of benzonorbornadiene, **8**, and **9** were almost invariable. The plausible mechanisms of the formation of bnd, **8**, and **9** are outlined in Scheme 5. First the pyridine ligand is thermally dissociated to produce the electron-deficient four-coordinate species **10**, in which the Pd−C and Pd−O bond scissions might occur to give rise to the zwitterionic intermediate **11**. Subsequently, the C−O bond cleavage along path a or the ring closure along path b would afford bnd and **8**, respectively. On the other hand, **11** is capable of isomerization to give an another zwitterionic intermediate **12,** and its ring closure gives rise to **9** (path c). The direct formation of **8** via reductive elimination is also possible, and alternatively, the thermal Diels−Alder cycloaddition of *o*-chloranil and benzonorbornadiene might produce **8**. In fact, heating the solution of 1 equiv each of benzonorbornadiene and *o*-chloranil in $CHCl_3$ at 70 °C for 12 h furnished **8** in 15% isolated yield.

The pyridine complex **7c** proved to be very sensitive toward a protic acid. When HCl was passed through a $CDCl_3$ solution at −40 to −50 °C, **7c** completely disappeared within 15 min to give benzonorbornadiene and the chlorinated product **13** (Scheme 6). The possible mechanism for the acid-promoted decomposition of **7c** is outlined in Scheme 6. The protonation of one of the two catechol oxygens might trigger the Pd−C bond

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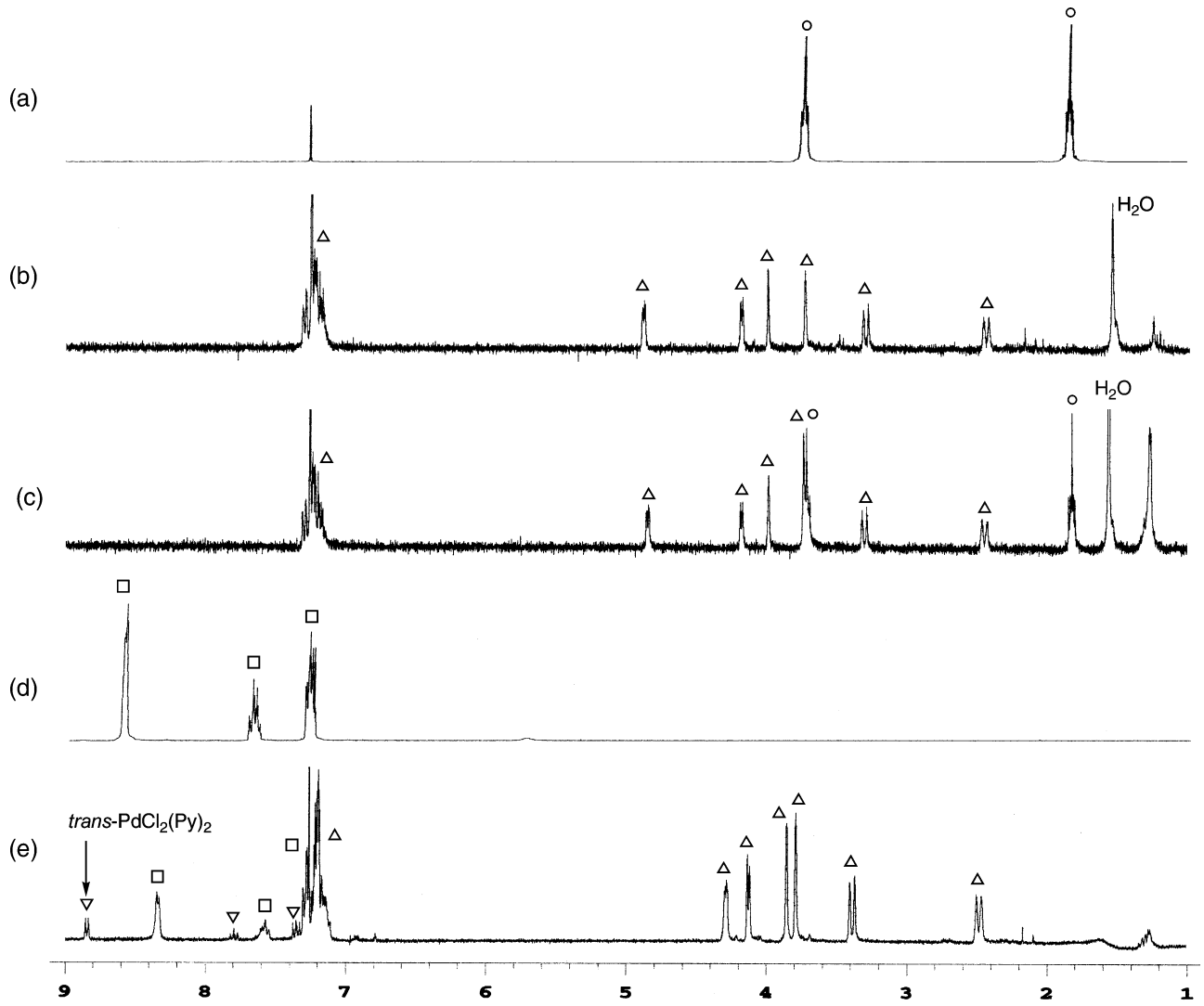


Figure 7. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of (a) THF, (b) **7a** after silica gel chromatography, (c) **7b**, (d) pyridine, and (e) **7c**.

cleavage. As a result, the cationic intermediate **14** could be produced, and its fragmentation leads to the formation of benzonorbornadiene and *o*-chloranil (path a). Alternatively, **14** is converted to the isomeric cation **15**, which is finally attacked by chloride ion to give **13** (path b). In contrast to the zwitterionic intermediates **11** and **12**, the cations **14** and **15** did not give the corresponding cyclization products. The structure of **13** was unambiguously determined by X-ray analysis, as shown in Figure 8.

Conclusion

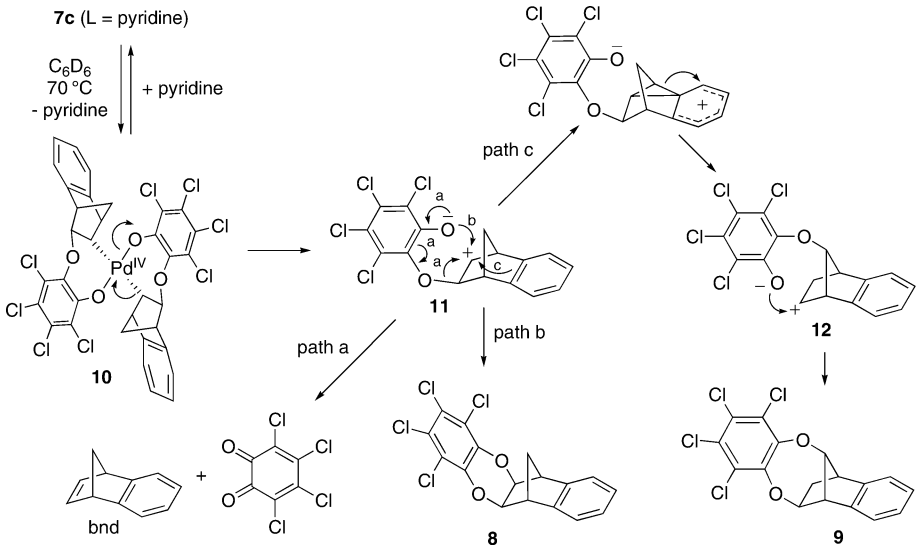
In conclusion, we have disclosed that the novel palladium(IV) complex can be assembled in a single step from the readily available $Pd_2(dba)_3$, *o*-chloranil, and norbornene. The structure consists of the C_2-symmetrical palladaspirocyclic framework and a Lewis base ligand, as confirmed by X-ray analysis of the THF and pyridine complexes. Employing benzonorbornadiene as an olefin component also produced a similar palladaspirocyclic framework, which has a greater stability compared to the parent one derived from norbornene. The thermolysis of the benzonorbornadiene-derived complex bearing one pyridine ligand shows that the palladaspirocycle decomposed over several hours at 70 °C to give rise to benzonorbornadiene as the main organic fragment. The thermal decomposition was retarded by adding extra pyridine, which hampers the formation of the less stable four-coordinate intermediate. It was also found that the palladaspirocycle is labile toward a protic acid. It decomposed within 15 min even at −40 °C, upon exposure to HCl in $CDCl_3$.

Experimental Section

General Considerations. ^{1}H and ^{13}C NMR spectra were obtained for samples in $CDCl_3$ solution at 25 °C. ^{1}H NMR chemical shifts are reported in δ units, in ppm relative to the singlet at 7.26 ppm for chloroform. Coupling constants are reported in hertz. Elemental analyses were performed by the Microanalytical Center of Kyoto University and the Instrumental Analysis Facility of Nagoya University. Melting points were obtained in capillary tubes and are uncorrected. Acetone was distilled from $CaSO_4$ and degassed. Flash chromatography was performed with a silica gel column (Merck silica gel 60) eluted with mixed solvents (hexane/AcOEt).

Synthetic Procedure for 4a. A solution of $Pd_2(dba)_3 \cdot CHCl_3$ (155.3 mg, 0.150 mmol), *o*-chloranil (245.9 mg, 0.750 mmol), and norbornene (94.2 mg, 0.750 mmol) in dry degassed acetone (10 mL) was stirred at room temperature for 30 min.

Scheme 5



pyridine / equiv	time / h	isolated yield (NMR yield) / %			
		trans-$PdCl_2(py)_2$	bnd	**8**	**9**
0	4	trace	(43)	12	4
1	6.5	(15)	(50)	15	7
5	50	47	(57)	14	6

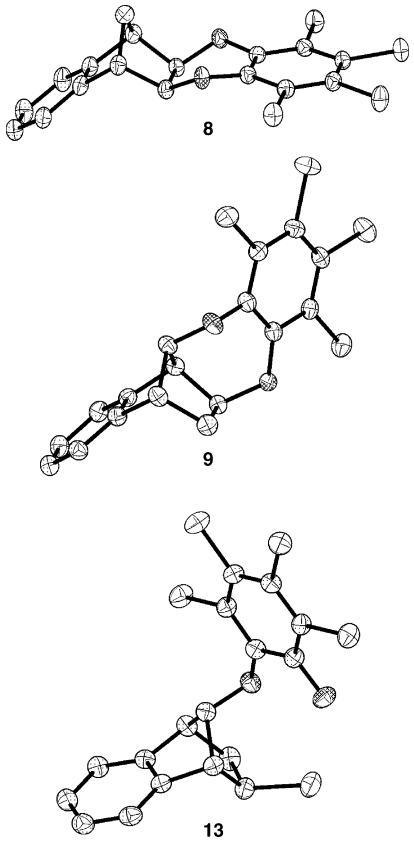


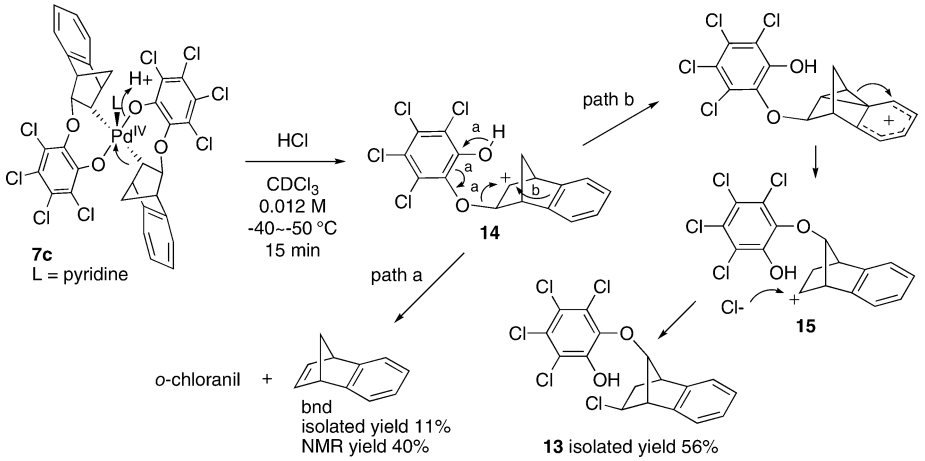
Figure 8. ORTEP diagrams of **8**, **9**, and **13**. All hydrogen atoms were omitted for clarity.

The initial purple suspension turned into a red homogeneous solution within 10 min. The resultant solution was filtered through a glass frit, and the filtrate was concentrated to 3 mL, diluted with dry degassed ether (50 mL), and cooled overnight at ca. −15 °C. The obtained orange crystals were collected on a glass frit and dried under vacuum at room temperature for 48 h. The yield was 209.9 mg (81%). Mp: 117.3−118.3 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.00−1.15 (m, 1 H), 1.21 (t, J = 7.0 Hz, 3 H), 1.35−1.46 (m, 1 H), 1.48−1.75 (m, 3 H), 2.66 (d, J = 4.5 Hz, 1 H), 2.84 (d, J = 4.5 Hz, 1 H), 3.01 (d, J = 11.5 Hz, 1 H), 3.48 (q, J = 7.0 Hz, 3 H), 4.08 (d, J = 4.5 Hz, 1 H), 4.84 (dd, J = 4.5, 2.0 Hz, 1 H). Anal. Calcd for $C_{30}H_{30}Cl_8O_5Pd$ (860.60): C, 41.87; H, 3.51. Found: C, 41.60; H, 3.53.

Synthetic Procedure for 4b. The ether complex **4a** (86.1 mg, 0.10 mmol) was dissolved in dry degassed THF (5 mL) and stirred at room temperature for 30 min. The solution was filtered through a glass frit, and the filtrate was concentrated to 1 mL, diluted with dry degassed pentane (10 mL), and cooled overnight at ca. −15 °C. The obtained orange crystals were collected on a glass frit and dried under vacuum at room temperature for 48 h. The yield was 82.4 mg (96%). Mp: 109.8−110.0 °C dec. ^{1}H NMR (500 MHz, THF-d_8): δ 1.20−1.27 (m, 1 H), 1.43−1.49 (m, 1 H), 1.54 (tt, J = 12.5, 5.0 Hz, 1 H), 1.65 (d, J = 11.0 Hz, 1 H), 1.76−2.66 (m, 4 H), 2.66 (d, J = 4.5 Hz, 1 H), 2.75 (d, J = 5.0 Hz, 1 H), 2.94 (d, J = 11.0 Hz, 1 H), 3.60−3.64 (m, 4 H), 4.10 (d, J = 4.5 Hz, 1 H), 4.42 (dd, J = 5.5, 2.5 Hz, 1 H). ^{13}C NMR (125 MHz, THF-d_8): δ 24.73 (CH_2), 26.39 (CH_2), 27.98 (CH_2), 36.67 (CH_2), 44.44 (CH), 45.83 (CH), 68.22 (CH_2), 78.12 (CH), 98.92 (CH), 117.85, 122.49, 124.87, 128.20, 144.76, 157.24. MS (FAB): m/z (%) 541 (44) [M^+ − THF − $C_6Cl_4O_2$], 446 (100) [MH^+ − THF − $C_6Cl_4O_2$ − C_7H_{12}]. Anal. Calcd for $C_{30}H_{28}Cl_8O_5Pd$ (858.58): C, 41.97; H, 3.29. Found: C, 42.27; H, 3.43.

Synthetic Procedure for 5. The ether complex **4a** (86.1 mg, 0.10 mmol) was dissolved in dry degassed pyridine (1 mL) and stirred at room temperature for 30 min. The solution was filtered through a glass frit, and the filtrate was diluted with dry degassed pentane (30 mL) and cooled overnight at ca. −15 °C. The obtained brown crystals were collected on a glass frit and dried under vacuum at room temperature for 48 h. The yield was 76.7 mg (75.6%). Mp 99.2−99.5 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.16−1.32 (m, 1 H), 1.34−1.46 (m, 1 H), 1.54−1.80 (m, 3 H), 2.71 (d, J = 3.8 Hz, 1 H), 2.75 (d, J = 3.8 Hz, 1 H), 3.00 (d, J = 10.2 Hz, 1 H), 4.03 (s, 2 H), 7.25 (dd, J = 7.8,

Scheme 6



4.2 Hz, 4 H), 7.67 (tt, J = 7.8, 1.5 Hz, 1 H), 8.51 (d, J = 4.2 Hz, 4 H). MS (FAB): m/z (%) 541 (34) [M^+ − 3Py − $C_6Cl_4O_2$], 446 (100) [MH^+ − 3Py − $C_6Cl_4O_2$ − C_7H_{12}]. Anal. Calcd for $C_{41}H_{35}Cl_8N_3O_5Pd$ (1023.78): C, 48.10; H, 3.45; N, 4.10. Found: C, 47.93; H, 3.41; N, 3.91.

Synthetic Procedure for 6. A solution of $Pd_2(dba)_3$·$CHCl_3$ (72.5 mg, 0.070 mmol), *o*-chloranil (71.8 mg, 0.350 mmol), and 1,4-dihydro-9-isopropylidene-1,4-methanonaphththalene (63.8 mg, 0.350 mmol) in dry degassed acetone (5 mL) was stirred at room temperature for 1 h. The initial purple suspension finally turned into an orange homogeneous solution. The resultant solution was filtered through a glass frit, and the filtrate was concentrated and diluted with ether to precipitate dibenzilideneacetone. After the precipitates were removed, the solution was again concentrated to give colorless solids. The pure crystals were obtained by recrystallization from AcOEt/hexane. The yield was 16.0 mg (33.7%). Mp: 189.4 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (s, 12 H), 1.60−1.65 (br s, 2 H), 3.81 (s, 4 H), 6.03 (s, 4 H), 7.10 (dd, J = 5.1, 3.3 Hz, 4 H), 7.34 (dd, J = 5.1, 3.3 Hz, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.39, 56.98, 104.22, 108.62, 124.80, 126.53, 144.98. MS (FAB): m/z (%) 680 (31) [M^+ − H], 645 (100) [M^+ − Cl]; Anal. Calcd for $C_{28}H_{30}Cl_2O_2Pd_2$ (682.28): C, 49.29; H, 4.43. Found: C, 49.16; H, 4.39.

Synthetic Procedure for 7a and 7b. A solution of Pd_2-$(dba)_3$·$CHCl_3$ (791.8 mg, 0.765 mmol), *o*-chloranil (1.834 g, 7.48 mmol), and benzonorbornadiene (1.104 g, 7.76 mmol) in dry degassed acetone (55 mL) was stirred at room temperature for 80 min. The reaction mixture was then cooled to −15 °C, and the resultant precipitates were collected on a glass frit and dried under vacuum at room temperature. The yield was 815.5 mg (57%). Mp: 159.1−160.7 °C dec. Anal. Calcd for $C_{37}H_{26}Cl_8O_5Pd$ (940.64): C, 47.24; H, 2.79. Found: C, 47.32; H, 2.72.

The reaction of $Pd_2(dba)_3$·$CHCl_3$ (414.0 mg, 0.402 mmol), *o*-chloranil (922.7 mg, 4.50 mmol), and benzonorbornadiene (376.6 mg, 4.00 mmol) was carried out in dry degassed THF (30 mL) at room temperature for 30 min. A similar workup and recrystallization from THF/pentane at −15 °C gave **7b** as red crystals. The yield was 541.1 mg (78.4%). Mp: 172.3−173.3 °C dec. Anal. Calcd for $C_{38}H_{28}Cl_8O_5Pd$ (954.67): C, 47.81; H, 2.96. Found: C, 48.10; H, 3.14.

The acetone and THF complexes **7a** and **7b** gave identical ^{1}H and ^{13}C NMR spectra, except for the absorption of free acetone or THF, because of the dissociation of these ligands in solution. The absorptions of the resultant four-coordinate complex were as follows. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.45 (d, J = 10.5 Hz, 2 H), 3.31 (d, J = 10.5 Hz, 2 H), 3.72 (s, 2 H), 4.00 (s, 2 H), 4.18 (d, J = 4.5 Hz, 2 H), 4.88 (dd, J = 4.5, 1.8 Hz, 2 H), 7.16−7.32 (m, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 47.22, 49.82, 50.05, 76.13, 97.58, 118.36, 121.41, 122.54, 123.65, 123.72, 127.94, 128.12, 129.26, 142.77, 143.76, 144.00, 155.78. MS (FAB): m/z (%) 881 (15) [MH^+], 741 (11) [MH^+ − $C_{11}H_{10}$], 636 (87) [M^+ − $C_6Cl_4O_2$], 494 (100) [M^+ − $C_6Cl_4O_2$ − $C_{11}H_{10}$].

Synthetic Procedure for 7c. To a solution of the four-coordinate complex (46.9 mg, 0.0531 mmol) in dry degassed $CHCl_3$ (12 mL) was added pyridine (4.30 μL, 0.0531 mmol). The solution was stirred at room temperature for 1 h. The solution was concentrated to 2 mL, diluted with dry degassed pentane (25 mL), and cooled overnight at ca. −15 °C. The obtained red crystals were collected on a glass frit and dried under vacuum at room temperature. The yield was 39.9 mg (78%). Mp: 134.0−138.0 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.54 (d, J = 10.5 Hz, 2 H), 3.45 (d, J = 10.5 Hz, 2 H), 3.85 (s, 2 H), 3.91 (s, 2 H), 4.19 (d, J = 5.1 Hz, 2 H), 4.35 (dd, J = 5.1, 1.8 Hz, 2 H), 7.19−7.36 (m, 10 H), 7.60−7.67 (m, 1 H), 8.38−8.43 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 47.18, 49.26, 51.34, 71.63, 93.30, 117.67, 121.67, 123.32, 123.78, 124.31, 127.35, 127.82, 138.46, 143.58, 143.94, 144.71, 147.76, 153.22, 155.50. MS (FAB): m/z (%) 881 (18) [MH^+ − C_5H_5N], 636 (100) [M^+ − C_5H_5N − $C_6Cl_4O_2$], 494 (82) [M^+ − C_5H_5N − $C_6Cl_4O_2$ − $C_{11}H_{10}$]. Anal. Calcd for $C_{39}H_{25}Cl_8NO_4Pd$ (961.66): C, 48.71; H, 2.62; N, 1.46. Found: C, 48.83; H, 2.73; N, 1.48.

Thermolysis of 7c in the Presence of Pyridine. A solution of **7c** (46.8 mg, 0.0487 mmol) and pyridine (19.7 μL, 0.244 mmol) in dry degassed C_6D_6 (10 mL) was heated at 70 °C for 50 h. After $(Me_3Si)_2O$ was added as an internal standard, the yield of benzonorbornadiene was estimated as 57% by ^{1}H NMR spectroscopy. The solution was then concentrated in vacuo. The silica gel column chromatography (hexane/AcOEt 100/0 to 50/1) of the residue afforded benzonorbornadiene (1.9 mg, 13%) as a colorless oil and **8** (5.6 mg, 14%) and **9** (1.1 mg, 6%) as colorless solids. Further elution with AcOEt gave *trans*-$PdCl_2(py)_2$ (7.6 mg, 47%).

Analytical data for 8. Mp: 187.0−188.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.15 (d, J = 9.9 Hz, 1 H), 2.54 (d, J = 9.9 Hz, 1 H), 3.73 (s, 2 H), 4.27 (d, J = 1.5 Hz, 2 H), 7.17 (dd, J = 5.1, 3.3 Hz, 2 H), 7.30 (dd, J = 5.1, 3.3 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.01, 45.41, 76.35, 116.37, 118.18, 120.95, 122.91, 138.08, 138.93. MS (EI): m/z (%) 388 (15) [M^+], 141 (40) [M^+ − H − $C_6Cl_4O_2$], 116 (100) [M^+ − H − $C_6Cl_4O_2$ − C_2H_2]. Anal. Calcd for $C_{17}H_{10}Cl_4O_2$ (388.07): C, 52.61; H, 2.60. Found: C, 52.60; H, 2.54.

Analytical Data for 9. Mp: 222.0−223.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.15 (dd, J = 13.5, 7.5, Hz, 1 H), 2.70−2.78 (m, 1 H), 3.74 (s, 1 H), 3.78−3.82 (m, 1 H), 4.67 (s, 1 H), 4.75−7.80 (m, 1 H), 7.23−7.29 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.38, 48.53, 49.44, 81.09, 89.57, 122.06, 122.57, 123.30, 125.10, 126.12, 127.10, 127.31, 128.12, 137.24, 141.45, 144.69, 146.30. MS (EI): m/z (%) 388 (40) [M^+], 141 (100) [M^+ − H −

$C_6Cl_4O_2$]. Anal. Calcd for $C_{17}H_{10}Cl_4O_2$ (388.07): C, 52.61; H, 2.60. Found: C, 52.51; H, 2.65.

Acid-Promoted Decomposition of 7c. HCl gas was introduced through a glass inlet to a solution of **7c** (95.2 mg, 0.0990 mmol) in $CDCl_3$ (8 mL) at −40 to −50 °C for 15 min. The initial red solution turned into a yellow solution. After $(Me_3Si)_2O$ was added as an internal standard, the yield of benzonorbornadiene was estimated as 40% by ^1H NMR spectroscopy. The solution was then concentrated in vacuo. The silica gel column chromatography (hexane/AcOEt 100/0 to 10/1) of the residue afforded benzonorbornadiene (3.2 mg, 11%) as a colorless oil and **13** (46.9 mg, 56%) as colorless solids.

Analytical Data for 13. Mp: 186.0−187.0 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 2.32 (dd, J = 13.2, 7.5 Hz, 1 H), 2.71 (dt, J = 13.2, 3.6 Hz, 1 H), 3.69 (s, 1 H), 3.77−3.79 (m, 1 H), 4.06 (ddd, J = 8.1, 3.9, 1.2 Hz, 1 H), 4.21 (s, 1 H), 7.17−7.23 (m, 4 H), 7.50 (br s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.90, 48.02, 55.10, 58.61, 93.65, 119.53, 122.14, 122.48, 123.41, 125.20, 127.29, 128.06, 128.69, 139.53, 141.98, 142.17, 146.48. MS (EI): *m*/*z* (%) 424 (5) [M^+], 247 (10) [$M^+ - C_{11}H_{10}Cl$], 141 (100) [$M^+ - Cl - C_6Cl_4O_2H$]. Anal. Calcd for $C_{17}H_{11}Cl_5O_2$ (424.53): C, 48.10; H, 2.61. Found: C, 48.05; H, 2.72.

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Supporting Information Available: Text and tables giving additional crystallographic data and CIF files giving X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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