Comparison of the Reactivities of Neutral and Cationic Organopalladium Complexes toward CO, Isocyanides, and Olefins

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Cationic solvent-coordinated organopalladium complexes $[PdR(solvent)(L)_2]^+A^-$ **2** (R = organic group, L = tertiary phosphine, A = counter anion such as BF_4, PF_6, and triflate) have been prepared by removal of the halide ligand X in neutral complexes, $[PdR(X)(L)_2]$ **1** with an equimolar amount of silver salt. The cationic complexes **2** show much greater rates of CO insertion than the parent neutral complexes **1**. Comparison of the reactivities of **2** and of the other cationic complexes $[PdMe(Y)(L)_2]^+$ (Y = strongly coordinating ligand such as tertiary phosphine, pyridine, and isocyanide) toward CO insertion indicates that availability of the site for incoming CO is a dominant factor in determining their reactivities. In contrast, insertion of isocyanides into Pd–C bond is not hindered by occupation of the vacant site in the organopalladium complexes. Successive hetero-insertions of isocyanide and CO into Me–Pd bond, i.e., CO insertion into the 1-iminoalkyl–Pd bond and isocyanide insertion into the acetyl–Pd, were realized. Olefins were found not to undergo the insertion into Pd–Me bond in phosphine-coordinated complexes, whereas insertion of methyl acrylate into the Me–Pd bond in a cationic complex having bipyridine ligand was observed.

The study of organopalladium complexes is vital for understanding and constructing palladium-catalyzed organic syntheses.[1] In the course of our study of the cationic organometallic compounds,[2,3] it was clarified that the remarkable effects of addition of silver salts on Heck arylation were attributable to the generation of the cationic organopalladium complexes.[4—6] Cationic organopalladium complexes $[PdRL_2]^+$ (R = aryl group, L = ligand) generated from the corresponding neutral complexes $[PdR(X)L_2]$ (X = halide) were found to be much more reactive toward olefin insertion and the β-hydrogen elimination than the parent neutral complexes.[3,7] The cationic organopalladium complexes have proved to play important roles in other catalytic reactions such as single and double carbonylation of aryl halides,[8] alternating copolymerization of olefin and carbon monoxide,[9] and olefin polymerization.[10] Regarding the alternating copolymerization of olefin and CO, the mechanism has been examined in detail[11] and the considerable refinement of the catalyst systems has been reported.[12]

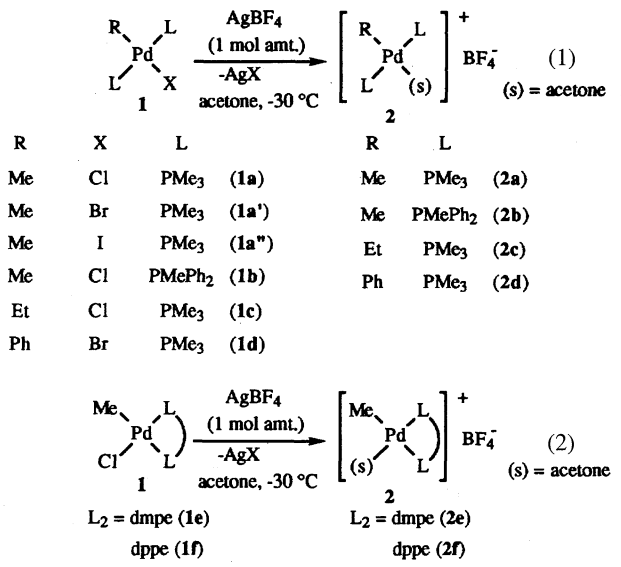
We previously reported the marked acceleration of CO insertion into palladium–carbon bond by generating cationic complexes from neutral complexes $[PdR(X)L_2]$ with silver salts.[13] A problem has remained whether the rate enhancement is caused by generation of electronically positive charge on the organopalladium complexes having possibly greater propensity toward coordination and the subsequent migratory insertion of CO, or it is due to the availability of a coordination site created by removal of the halide ligand. We report herein the synthesis and the comparison of the reactivities of several neutral and cationic organopalladium complexes as an attempt to address the problem.

The second objective of the present study is the comparison of reactivity of these neutral and cationic organopalladium complexes toward isocyanides. Isocyanides, being isoelectronic with carbon monoxide,[14] show coordination ability toward the vacant site in organopalladium complexes and undergo the subsequent insertion into a Pd–C bond. The insertion ability of isocyanides differs from that of CO insertion. In contrast to the carbon monoxide, for which consecutive CO insertion is disfavored,[15,16] isocyanides readily undergo the consecutive multiple insertion processes, which may lead to new types of organic compounds difficult to synthesize by other methods.[14,17]

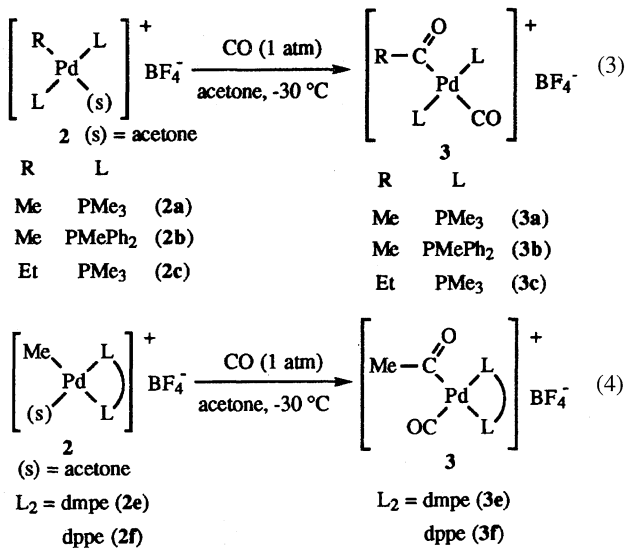
Thirdly we wanted to gain information concerning the factors controlling olefin insertion into a Pd–C bond. Despite the importance of the insertion of olefins into alkyl–palladium bond, studies clarifying the reaction courses of olefin insertion into neutral and cationic organopalladium complexes are quite limited.[18] We include here the results of our studies on the olefin insertion into Pd–C bond and compare the results with those of CO and isocyanide insertions.

Results

Synthesis of Cationic Complexes. Various cationic organopalladium complexes **2** have been generated by treatment of neutral monoorganopalladium halide complexes **1** with an equimolar amount of $AgBF_4$ in acetone at −30 °C. The cationic complexes **2a—2d** having monodentate phosphine ligands were found to retain the *trans* configurations of the starting neutral complexes, as confirmed by NMR. Particularly diagnostic of the *trans* configuration is the virtual triplets in the ^1H and ^{13}C NMR spectra and sin-



Scheme 1.

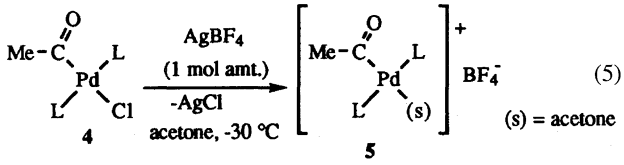


Scheme 2.

glet for the ^{31}P NMR of the methyl-containing phosphine ligands. The cationic *cis* complexes, **2e** and **2f**, having the chelate phosphine ligands were similarly prepared from the corresponding neutral complexes. Methyl complexes, **2a**, **2e**, and **2f**, were isolated as acetone-coordinated complexes, whose ^{1}H NMR in acetonitrile-d_3 showed a signal arising from the acetone. The stretching vibration of the carbonyl group ($\nu_{C=O}$) in the solvated acetone was also observed at 1636 cm^{-1} in the IR spectrum of **2a**.

The cationic complexes **2a**—**2f** are stable below −10 °C, but they decompose readity at room temperature. As previously reported,[19] the ethylpalladium complex **2c** having β-hydrogens decomposes with evolution of ethylene and ethane (1 : 1) at 20 °C. Ethane and methane (1 : 1—1 : 2.5) were generated from the methyl complexes **2a**, **2b**, **2e**, and **2f** while biphenyl and benzene were liberated from the cationic phenylpalladium complex **2d**. The proton source for formation of methane and benzene may be the solvent.[20] The decomposition pattern of the cationic methylpalladium complexes **2a** and **2b** having the trimethylphosphine ligands seems to differ from that of the cationic methylbis(triphenylphosphine)-palladium complex, $[PdMe(PPh_3)_2(CD_3CN)]^+BF_4^-$, which liberated the phosphonium salt $PPh_3Me^+BF_4^-$ by combination of the PPh_3 released with the methyl cation, as reported by Sen.[21]

CO Insertion into Alkylpalladium Complexes. The CO insertion into cationic alkylpalladium complexes **2a**—**2c**, **2e**, and **2f** gave acyl(carbonyl)palladium complexes **3a**—**3c**, **3e**, and **3f** under mild conditions (1 atm, −30 °C). The CH_3 signal of **2a** in ^{1}H NMR shifted from 0.49 to 2.54 ppm by formation of the acetyl complex **3a** under CO atmosphere. Since the ^{1}H NMR spectrum of $[Pd(CH_3C(O))(CO)(PMe_3)_2]^+BF_4^-$ **3a** was similar to that of cationic solvent-coordinated acetylpalladium complex, $[Pd(CH_3C(O))(acetone)(PMe_3)_2]^+BF_4^-$ **5**, derived from $[Pd(CH_3C(O))(Cl)(PMe_3)_2]$ **4** by treatment with an equimolar amount of $AgBF_4$, the coordination of the CO ligand to the Pd center was confirmed by ^{13}C NMR resonance at 181 ppm appeared as a triplet on treating **2a** with ^{13}C-labelled CO.



The conversion of the alkyl complexes (**1a** and **2a**—**2c**, **2e**, and **2f**) into the acyl complexes (**4** and **3a**—**3c**, **3e**, and **3f**) as followed by ^{1}H NMR showed the pseudo-first order kinetics. Figure 1 shows the first order plots for the formation of the cationic acetylpalladium complex **3a** from the cationic methylpalladium complex **2a** under CO atmosphere in several solvents at −10 °C. These results indicate that the strongly coordinating solvent tends to retard the CO insertion.

The observed rate constants for the conversion of the neutral and the cationic alkylpalladium complexes are listed in Table 1. The CO insertion rate constant of the cationic complex **2a** (k_{obsd}=2.3×10^{-4} s^{-1}) was found to be 10^2 times greater than that of the neutral complex **1a** (k_{obsd}=2.5×10^{-6} s^{-1}) at −20 °C. The rate of CO insertion of the methyl complex **2a** (k_{obsd}=2.3×10^{-4} s^{-1}) was slightly larger than that of the ethyl complex **2c** (k_{obsd}=1.7×10^{-4} s^{-1}). Further rate enhancement was observed by changing the geometry from the cationic *trans* complex **1a** to the cationic *cis* complexes **2e** and **2f** containing the chelate ligands.[22] The cationic $PMePh_2$-coordinated methylpalladium complex **2b** was more reactive toward CO (k_{obsd}=5.8×10^{-4} s^{-1} at −20 °C) than the PMe_3-coordinated complex **2a** (k_{obsd}=2.3×10^{-4} s^{-1}).

Synthesis of Cationic Complexes Having Various Trans Ligands and Their Reactivities for CO Insertion. In

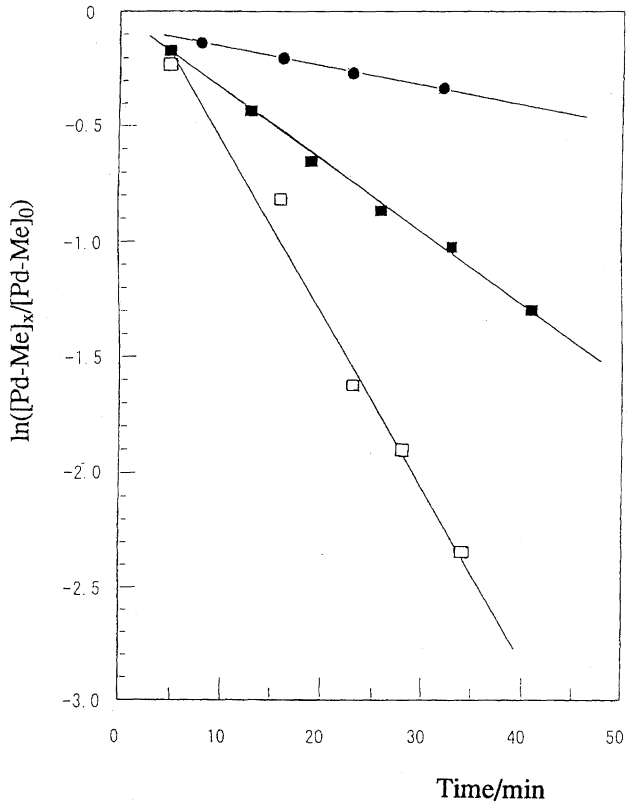


Fig. 1. Typical first-order plots for CO insertion into the cationic methylpalladium complex **2a** at −10 °C in acetonitrile-d_3 (●, $k_{obsd}=1.4\times10^{-4}$ s^{-1}), acetone-d_6 (■, $k_{obsd}=5.1\times10^{-4}$ s^{-1}), and dichloromethane-d_2 (□, $k_{obsd}=1.3\times10^{-3}$ s^{-1}) under CO atmosphere.

order to clarify the influence of the ligand bound *trans* to the alkyl and aryl groups on the reactivities for the CO insertion, other cationic organopalladium complexes **6** were prepared by addition of ligand Y to the solvent-coordinated cationic complexes **2a** and **2d**. In contrast to the cationic organopalladium complexes coordinated with acetone at the *trans* position, the cationic organopalladium complexes having strongly coordinating ligands such as trimethylphosphine, pyridine, and isocyanides **6a—6f** are stable even at room temperature. As can be seen from Table 1, increase in the coordinating ability of the ligand *trans* to the methyl ligand in **6** retarded the CO insertion, but the CO insertion was not blocked at −20 °C under atmosphere of CO.

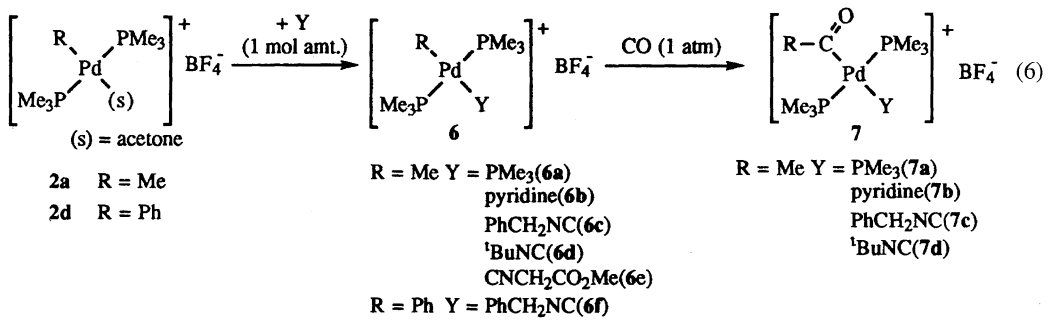
Influence of Counter Anions on the Rate of CO Insertion into the Cationic Methylpalladium Complex. The nature of the counter anion associated with the cationic organopalladium complex also affects the CO insertion rate. Table 2 shows the rate constants for CO insertion into cationic methylpalladium complexes that were generated on treatment of **1a** with several silver salts. The counter anion BF_4^- of the cationic complex **2a** is considered to have no interaction with the palladium center, since the four fluorine nuclei in BF_4 were observed as equivalent in the ^{19}F NMR. The PF_6^- containing complex showed similar reactivity toward CO insertion with the complex having BF_4^- counter anion. On the other hand, use of OTf^- or NO_3^- caused a decrease in the reactivity toward CO insertion.[23]

Table 2. Effects of Silver Salts on the Rate of CO Insertion of **1a** (s^{-1}) (−20 °C, acetone-d_6)

Counter anion	Rate k_{obsd}/s^{-1}
BF_4	2.3×10^{-4}
PF_6	2.4×10^{-4}
OTf	1.1×10^{-4}
NO_3	5.9×10^{-5}

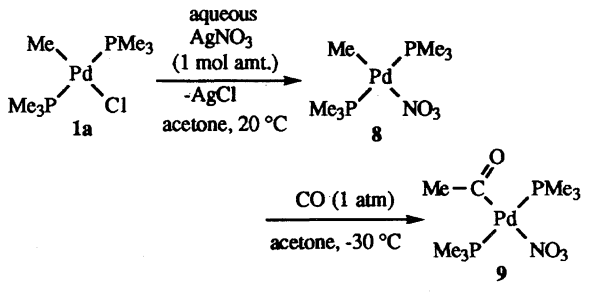
Table 1. Rate of CO Insertion into Methylpalladium Complexes (s^{-1}) (−20 °C, acetone-d_6)

Run	Methylpalladium complex		Rate k_{obsd}/s^{-1}
1	*trans*-[PdMe(Cl)(PMe_3)$_2$]	**1a**	2.5×10^{-6}
2	*trans*-[PdMe(acetone)(PMe_3)$_2$]$^+BF_4^-$	**2a**	2.3×10^{-4}
3	*trans*-[PdMe(acetone)($PMePh_2$)$_2$]$^+BF_4^-$	**2b**	5.8×10^{-4}
4	*trans*-[PdEt(acetone)(PMe_3)$_2$]$^+BF_4^-$	**2c**	1.7×10^{-4}
5	*trans*-[PdMe($CNCH_2Ph$)(PMe_3)$_2$]$^+BF_4^-$	**6c**	3.3×10^{-7}
6	*trans*-[PdMe(CN^tBu)(PMe_3)$_2$]$^+BF_4^-$	**6d**	2.3×10^{-7}



Scheme 3.

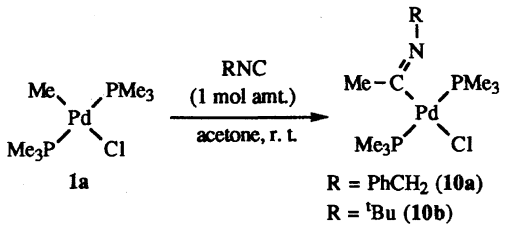
Synthesis of Methyl(nitrato)palladium Complex and Its Reactivity for CO Insertion. Methyl(nitrato)palladium complex **8** was prepared by treatment of **1a** with an equimolar amount of aqueous $AgNO_3$. Bonding of the nitrato ligand to palladium giving the neutral complex was confirmed by low conductivity values in non-aqueous solvents, whereas dissociation of the nitrate ion was observed in the aqueous solution (Table 3). The transformation of **8** into the acetyl complex **9** under atmospheric CO proceeded at −30 °C in acetone.



(7)

Addition of water to the acetone solution (1 : 1) of **8** was found to accelerate the CO insertion rate from 8.4×10^{-5} without water to 1.9×10^{-4} s^{-1} at −10 °C. In a water-containing solution, **8** may form a water-coordinated cationic complex which shows higher reactivity toward CO than the neutral NO_3-bound complex.

Isocyanide Insertion into the Neutral and Cationic Complexes. Benzyl isocyanide and *t*-butyl isocyanide inserted into the Pd–C bond of the neutral complex **1a** at ambient temperature to give 1-iminoethyl palladium complexes **10a** and **10b**, similarly to the results already reported.[24]

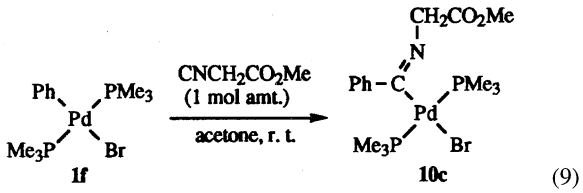


(8)

Methyl isocyanoacetate, being less reactive than the benzyl and *t*-butyl isocyanides, did not react with the neutral methylpalladium complex, whereas the corresponding phenyl complex **1d** were found to be more susceptible to the isocyanide insertion to give the 1-iminobenzylpalladium complex **10c** at room temperature.

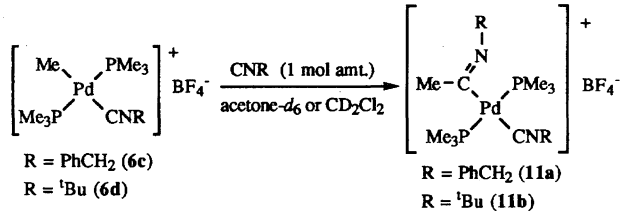
Table 3. Molar Conductivity of **8** in Several Solvents at 297 K ($\times$S cm^2 mol^{-1})

Solvent	Molar conductivity
Acetone	5.99
CH_2Cl_2	8.13
H_2O	1.33×10^2



(9)

As shown in Eq. 6, treatment of the cationic complex **2a** with an equimolar amount of isocyanides gave isocyanide-coordinated complexes **6c**—**6e** without affording the insertion products at 60 °C. Although heating the isocyanide-coordinated complexes **6c**—**6e** did not convert them into 1-iminoalkylpalladium complexes through isocyanide insertion, addition of one more molar amount of benzyl isocyanide and *t*-butyl isocyanide to **6c** and **6d**, respectively, afforded the corresponding 1-iminoethyl complexes **11** coordinated with the isocyanide (Eq. 10).



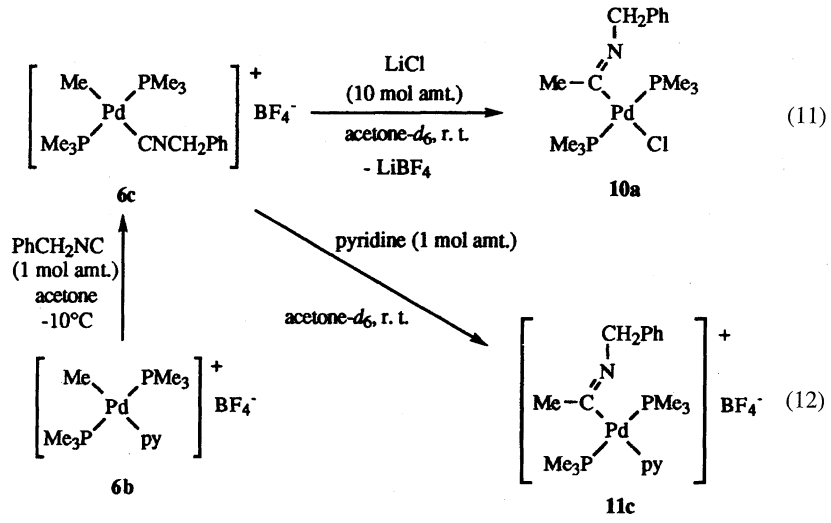
(10)

But the less reactive isocyanide, methyl isocyanoacetate, did not react with **6e** at all.

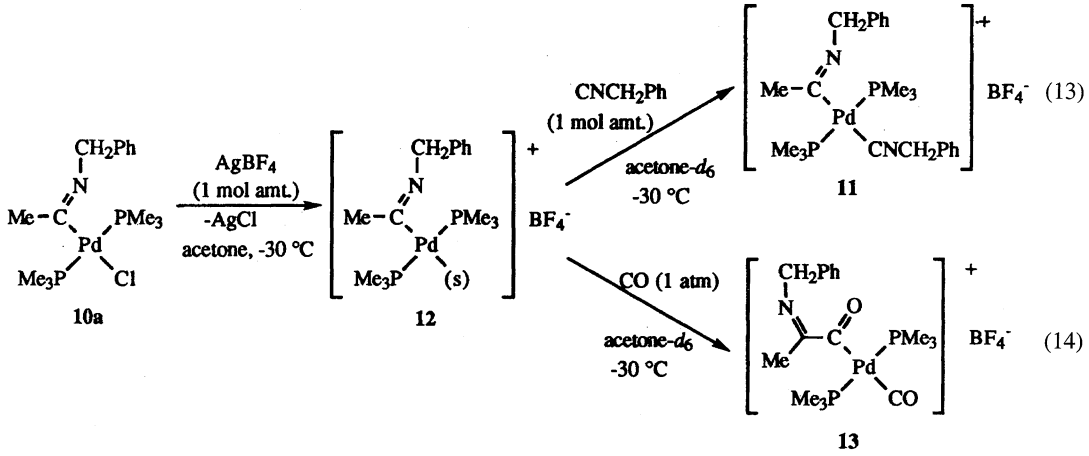
Treatment of the cationic pyridine-coordinated complex **6b** with an equimolar amount of benzyl isocyanide provides the isocyanide-coordinated complex **6c** immediately at −10 °C without giving the isocyanide insertion product **11c**. Addition of LiCl (10 mol amt.) or pyridine (1 mol amt.) to **6c** at room temperature caused insertion of the benzylisocyanide into the Me–Pd bond to give 1-iminoethylpalladium complex **10a** or **11c**.

Treatment of the Neutral 1-Iminoalkylpalladium Complex with Silver Salts. For elucidation of the stability of the 1-iminoalkyl complexes, the neutral 1-iminoethyl complex **10a** was treated with an equimolar amount of $AgBF_4$ to generate cationic complex **12**. The 1-iminoethyl complex **12** reacted with an equimolar amount of benzyl isocyanide to give the corresponding adduct, **11a**. The cationic complex **12** was stable and no deinsertion of the isocyanide entity proceeded at −30 °C.

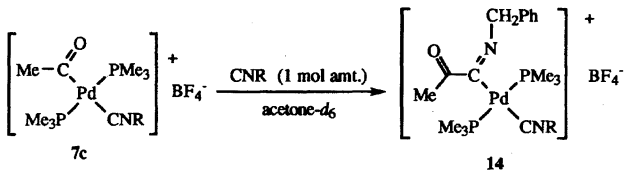
The cationic 1-iminoethylpalladium complex **12** provided further the CO-inserted product **13** under CO atmosphere at −30 °C (Eq. 14). On the other hand, slow insertion of benzyl isocyanide into the cationic acyl–palladium complex **7c** also took place to give **14** (Eq. 15). It is noteworthy that both types of consecutive hetero insertions of the isoelectronic unsaturated compounds were observed, i.e., the isocyanide insertion into the acyl–palladium bond (**7c** to **14**) and the CO insertion into 1-iminoethyl–palladium bond (**12** to **13**).



Scheme 4.

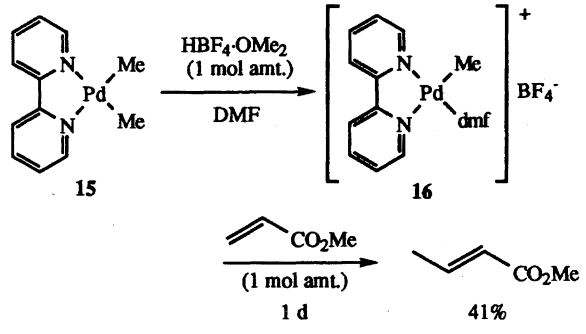


Scheme 5.



(15)

Olefin Insertion into the Pd–Me Bond. We next examined the reaction of the neutral and the cationic methylpalladium complexes with methyl acrylate by means of ^{1}H NMR. Although the cationic PMe_3-coordinated phenylpalladium complex reacted with styrene and methyl acrylate to liberate stilbene and methyl cinnamate, respectively, the phosphine-coordinated methylpalladium complexes prepared in the present study proved unreactive toward olefins. Therefore, we tried to prepare pyridine- and 2,2′-bipyridine (bpy)-coordinated dimethylpalladium complexes and their respective cationic monomethylpalladium complexes to examine their reactivities toward olefins. $[PdMe_2(py)_2]$ could be prepared, but it turned out to be too unstable for further studies.[25] The cationic complex $[PdMe_2(dmf)(bpy)]^+BF_4^-$ **16** was prepared by treatment of $[PdMe_2(bpy)]$ **15** with an equimolar amount of HBF_4·OMe_2 in *N*,*N*-dimethylformamide (DMF). The reaction of **16** with methyl acrylate in DMF-d_7 at room temperature for 1 d gave methyl crotonate in a yield of 41%, as confirmed by ^{1}H NMR.



(16)

Discussion

Factors Controlling the Reactivity for CO Insertion into Monomethyl–Palladium Complexes. The results obtained in the present study indicate that the reactivity of organopalladium complexes for insertion of CO, isocyanides, and olefins varies depending on the substrates to undergo the insertion. Removal of the halide ligand in *trans*-monoorganobis(trimethylphosphine)palladium halides **1a—1c** to give the cationic complexes **2a—2c** caused a marked rate increase in the CO insertion rate (by a factor of 10^2 by converting **1a** into **2a**). The results suggest that the enhancement in the reactivity was caused by creating the cationic center for CO coordination and the subsequent insertion. However, by replacing the coordination site *trans* to the methyl ligand by strongly coordinating ligands such as PMe_3 and isocyanides, the CO insertion rate is decreased below that of the neutral complex, **1a**, as can be seen from the results in Table 1. Such results show that it is the availability of a coordination site in the square planar monoorganopalladium complex and not the generation of a cationic complex that determines the reactivity for the CO insertion. The results shown in Fig. 1 also indicate that the solvent of higher coordinating ability tends to diminish the reactivity toward CO insertion, as observed in the order of acetonitrile > acetone > dichloromethane. As shown in Table 2, the nature of the counter anion also influences the reactivity for the CO insertion. While the BF_4 and PF_6 anions behave as non-interacting anions, the presence of the triflate, which is usually considered as a non-interacting anion,[26] causes some lowering in the reactivity for the CO insertion. The nitrate coordinates more strongly to the cationic palladium center to form a neutral complex in acetone and lowers the reactivity of the methylpalladium complex toward CO (Table 2). The reaction of the NO_3-coordinated neutral complex toward CO proceeds much faster in water-containing solution, where the NO_3-coordinated complex **8** shows a much greater conductivity than in acetone or dichloromethane (Table 3). This result suggests that in certain cases the availability of the coordination site for CO is increased by carrying out the process in water. The observation may be related with higher catalytic carbonylation activities when the reaction is carried out in water solution or two-phase media (water and organic solvents).[27]

For the cationic, solvent-coordinated *trans*monoorganobis(tertiary phosphine)palladium complexes **2a—2c** to undergo the migratory CO insertion, they are considered to be isomerized first to *cis* complexes.[28] In agreement with the assumption of the *cis* migratory insertion,[29] the cationic *cis* complexes **2e** and **2f** having the chelate ligands and a coordination site available adjacent to the methyl ligand for the incoming CO showed the higher reactivity than the *trans* complex **2a**. For the *trans* to *cis* isomerization to take place, migration of the tertiary phosphine ligand from the position *cis* to the methyl ligand to the site *trans* to the methyl is required. The reason why the $PMePh_2$-coordinated complex **2b** showed the higher reactivity than the PMe_3-coordinated complex **2a** may be ascribed to the weaker coordinating ability of $PMePh_2$ than PMe_3 to enable the ligand migration (Runs 2 and 3 in Table 1).

Comparison of CO and Isocyanide Insertions into the Pd–C Bond. In contrast to the reactivity pattern of the monoorganopalladium complexes toward CO, whose reactivity was increased by creation of a vacant coordination site in the square planar environment for the incoming CO, the reactivity pattern for isocyanides showed considerable variance. The isocyanide insertion into the neutral methylpalladium complex **1a** was observed to take place readily at room temperature (Eq. 8). Addition of an equimolar amount of isocyanides to the cationic, acetone-coordinated monoorganopalladium complexes **2a** and **2d** gave simple isocyanide adducts **6c—6f** without giving the 1-iminoalkyl complexes as the insertion products. This is in contrast to the reaction of **2a** with CO, which readily gave acetylpalladium complex **3** on reaction with the cationic methylpalladium complex **2** at −30 °C without giving the CO-coordinated methylpalladium species. Whereas the isocyanide coordination in **6c** and **6d** decreased the CO insertion rate by a factor of 10^3 than the acetone-coordinated methylpalladium complex **2a** (Table 1), the presence of the isocyanide ligand *trans* to the methyl ligand in **6c** and **6d** did not block the isocyanide insertion but gave the isocyanide-coordinated 1-iminoethyl complexes **11** (Eq. 10). Such results, implying that a vacant site in the square plane is not required for the isocyanide insertion, suggest operation of a different mechanism for the isocyanide insertion from that for CO insertion, possibly involving a five-coordinate intermediate. The promotion of the isocyanide insertion into the Me–Pd bond in the isocyanide-coordinated cationic methylpalladium complex **6c** by addition of pyridine or chloride anion to give **10a** and **11c** (Eqs. 11 and 12) may be also accounted for by a mechanism involving the five-coordinate intermediate.

The reaction of the cationic isocyanide-coordinated complex **6c** or **6d** with CO afforded the corresponding isocyanide-coordinated acylpalladium complexes **7c** and **7d** without formation of 1-iminoethylpalladium complexes (Eq. 6). The result may suggest that the propensity of the CO toward insertion into the Pd–C bond is higher than that of the isocyanides.[30]

The isocyanides are known to undergo the successive insertions into a Pd–C bond,[14,15,24] whereas the successive CO insertion is known to be thermodynamically and kinetically unfavorable. A noteworthy feature of the present study is the observation of successive hetero-insertion of the isocyanides and CO into a Pd–C bond. The results imply that the deinsertion of either CO or isocyanide is not involved during these insertion processes.[31] To our knowledge, this is the first example of observation of the successive hetero-insertions.

Olefin Insertion into the Pd–Me Bond. In the Heck type reactions of olefin arylation or vinylation reactions, olefin insertion into the Pd–aryl or Pd–vinyl bond constitutes the key elementary step. In our previous study[3] on the reactivity of organopalladium complexes, we observed that the reactivity

of *trans*-[PdPh(Br)(PMe_3)$_2$] **1d** having Pd–C(sp^2) bond toward olefin insertion was markedly enhanced by converting it into the cationic complex **2d**. However, the methylpalladium complexes having Pd–C(sp^3) bond and tertiary phosphine ligands were found inactive for the olefin insertion, regardless whether they are neutral or cationic. In contrast, the bipyridine-coordinated methylpalladium complex **16** in a cationic form having a coordination site in the square plane showed reactivity to the olefin insertion (Eq. 16). The result is in line with the demonstrated activities of the palladium catalyst having the nitrogen base ligands for the polymerization of ethylene.[18b]

Conclusions

(1) The cause of the enhancement in reactivity of organopalladium complexes toward CO insertion by converting the neutral monoorganopalladium halide complexes into cationic complexes by removal of the halide ligand was found to be mainly due to the generation of a coordination site available for the incoming CO to undergo the *cis* alkyl migration in the square planar geometry. (2) In contrast, insertion of isocyanides into Pd–alkyl bond was not inhibited by the occupation of the site for the isocyanide coordination in the square planar geometry, suggesting the operation of a mechanism via five-coordinate intermediates. (3) Heterosuccessive insertions of isocyanides and CO into a Pd–C bond observed in the present study have few precedents, whereas successive CO insertion into Pd–C bond is energetically unfavorable and the successive homo-insertion of isocyanides into Pd–C bond are well-known. (4) Olefin insertion into Pd–C(sp^3) bond, which was not observed with tertiary phosphine ligand, was realized by generation of a cationic methylpalladium complex having a nitrogen base ligand.

Experimental

General Procedures. All the manipulations were performed under argon atmosphere by using Schlenk techniques. [PdMe(Cl)(dppe)],[22a] [PdEt(Cl)(PMe_3)$_2$],[19,32] and [$PdCl_2$(bpy)][33] were synthesized by the literature methods. [Pd(acac)$_2$] was prepared by treating [Na_2PdCl_4] with acetylacetone and aqueous NaOH. ^{13}C-labelled-carbon monoxide was purchased from Isotec Inc. and used without further purification. All the phosphines and the other reagents were used as received from commercial suppliers. Solvents were dried, distilled, and stored under argon. ^{1}H (270 MHz, referenced to $SiMe_4$ via residual solvent protons), ^{13}C{^{1}H} (67.9 MHz, referenced to $SiMe_4$ via the solvent resonance), ^{31}P{^{1}H} (109.4 MHz, referenced to 85% H_3PO_4 as an external standard), and ^{19}F (254.2 MHz, referenced to CF_3COOH as an external standard) NMR were recorded on a JEOL EX-270 spectrometer. Coupling constants (*J* values) are given in hertz (Hz), and spin multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), m (multiplet), vt (virtual triplet), and br (broad). Elemental analyses were carried out using a Yanako MT-3. Conductivities were measured by using a Denki Kagaku Keiki AOC-10 conductometer thermostatted at 298 K.

Preparation of Methyl(halo)palladium Complexes [PdMe(X)L$_2$] (X=Halide, L=Phosphine Ligands) (1a—c). The same procedure used for the preparation of [PdEt(Cl)(PMe_3)$_2$] was applied, i.e., the exchange of the acetato ligand in [PdMe(OAc)L$_2$] with halide X in LiX was carried out. A typical procedure is as follows.[19] Acetic acid (280 μl, 4.9 mmol) was added to a CH_2Cl_2 (9 mL) solution of *trans*-[$PdMe_2$(PMe_3)$_2$] (1.256 g, 4.4 mmol) at −30 °C. Stirring the reaction mixture for 30 min gave a colorless solution. An aqueous lithium chloride (210 mg, 5.0 mmol) solution (4 mL) was added to the reaction mixture at 0 °C. After stirring for 2 h, the yellow CH_2Cl_2 layer was evaporated to give white solids of *trans*-[PdMe(Cl)(PMe_3)$_2$] which were recrystallized from Et_2O.

***trans*-[PdMe(Cl)(PMe_3)$_2$] (1a):** Yield 78%, colorless crystals. ^{1}H NMR (acetone-d_6, −30 °C) δ=1.38 (18H, P(CH_3)$_3$, vt, J_{PH}=3.3 Hz), 0.20 (3H, PdCH_3, t, $^3J_{PH}$=6.7 Hz); ^{31}P{^{1}H} NMR (acetone-d_6, −30 °C) δ=−13.4 (s); ^{13}C{^{1}H} NMR (acetone-d_6, −30 °C) δ=13.9 (P(CH_3)$_3$, vt, J_{PC}=14.5 Hz), −7.8 (PdCH_3, t, $^2J_{PC}$=5.3 Hz). Anal. Found: C, 27.26; H, 7.03%. Calcd for $C_7H_{21}ClP_2Pd$: C, 27.20; H, 6.85%.

***trans*-[PdMe(Br)(PMe_3)$_2$] (1a′):** Yield 48%, yellow powder. ^{1}H NMR (acetone-d_6, −30 °C) δ=1.40 (18H, P(CH_3)$_3$, vt, J_{PH}=3.1 Hz), 0.30 (3H, PdCH_3, t, $^3J_{PH}$=6.5 Hz). Anal. Found: C, 23.59; H, 6.33%. Calcd for $C_7H_{21}BrP_2Pd$: C, 23.78; H, 5.99%.

***trans*-[PdMe(I)(PMe_3)$_2$][34] (1a″):** Yield 70%, yellow powder. ^{1}H NMR (acetone-d_6, −30 °C) δ=1.36 (18H, P(CH_3)$_3$, vt, J_{PH}=3.5 Hz), 0.49 (3H, PdCH_3, t, $^3J_{PH}$=7.0 Hz); ^{31}P{^{1}H} NMR (acetone-d_6, −30 °C) δ=−18.0 (s).

***trans*-[PdMe(Cl)($PMePh_2$)$_2$] (1b):** Yield 82%, white powder. ^{1}H NMR (acetone-d_6, −30 °C) δ=7.7—7.4 (20H, P$Me(C_6H_5)_2$, m), 2.15 (6H, P(CH_3)Ph_2, vt, J_{PH}=2.9 Hz), −0.13 (3H, PdCH_3, t, $^3J_{PH}$=6.0 Hz); ^{31}P{^{1}H} NMR (acetone-d_6, −30 °C) δ=16.1 (s). Anal. Found: C, 58.11; H, 5.26%. Calcd for $C_{27}H_{29}ClP_2Pd$: C, 58.19; H, 5.24%.

[PdMe(Cl)(dmpe)] (1e): Yield 54%, white powder. ^{1}H NMR (acetone-d_6, −30 °C) δ=2.2—1.7 (4H, $Me_2PC_2H_4PMe_2$, m), 1.63 (6H, P(CH_3)$_2$, d, J_{PH}=11.0 Hz), 1.41 (6H, P(CH_3)$_2$, d, J_{PH}=9.2 Hz), 0.27 (3H, PdCH_3, dd, $^3J_{PH}$=3.4, 8.4 Hz). Anal. Found: C, 27.64; H, 6.28%. Calcd for $C_7H_{19}ClP_2Pd$: C, 27.45; H, 6.26%.

Preparation of *trans*-[PdPh(Br)(PMe_3)$_2$] (1d). The same procedure as used for the preparation of [PdPh(Br)($PMePh_2$)$_2$] was employed.[35] Yield: 47%, pale-yellow crystals. ^{1}H NMR (acetone-d_6, −30 °C) δ=7.24 (2H, *o*-Ph, d, $^2J_{HH}$=7.0 Hz), 7.01 (2H, *m*-Ph, dd, $^2J_{HH}$=7.0 and 7.3 Hz), 6.87 (1H, *p*-Ph, t, $^2J_{HH}$=7.3 Hz), 1.17 (18H, P(CH_3)$_3$, vt, J_{PH}=3.3 Hz); ^{31}P{^{1}H} NMR ($CDCl_3$, −30 °C) δ=−17.0 (s). Anal. Found: C, 34.62; H, 5.70%. Calcd for $C_{12}H_{23}BrP_2Pd$: C, 34.68; H, 5.58%.

Preparation of *trans*-[Pd($CH_3C(O)$)(Cl)(PMe_3)$_2$] (4). The same procedure used for the preparation of [PdPh(Br)($PMePh_2$)$_2$] gave **4** in 52% yield as a white powder. NMR data for *trans*-[Pd($CH_3C(O)$)(Cl)(PMe_3)$_2$] was already reported.[13a]

Preparation of [PdMe(acetone)(L)$_2$]$^+BF_4^-$ (L=Phosphine Ligands) (2). *trans*-[PdMe(acetone)(PMe_3)$_2$]$^+BF_4^-$ (2a): To a CH_2Cl_2 (8 mL) solution of *trans*-[PdMe(I)(PMe_3)$_2$] (333 mg, 0.829 mmol) was added $AgBF_4$ (162 mg, 0.832 mmol) in 1 mL of acetone at −40 °C. A yellow suspension was formed immediately. The solution was stirred for 10 min and the silver iodide was removed by filtration to give a clear solution. The solution was reduced in volume to ca. 3 mL and it was then treated with toluene (10 mL). After standing for 1 week at −30 °C, the precipitate was collected by filtration. The white powder was washed with pentane (3 mL×2) and dried in vacuo. Yield: 142 mg (41%), white powder. The dmpe- or dppe-coordinating cationic complex could be prepared in similar procedures as above. For **2e**: yield 48%, white powder. For **2f**: yield 75%, white powder. The isolated complexes **2a**, **2e**, and **2f** were not stable enough to be subjected to elemental analysis.

The spectroscopic data for **2a**, **2e**, and **2f** were already reported.[13a)]

Generation of the Cationic Complexes 2 in NMR Tube. To a solution containing complex **1** in acetone-d_6 (0.35 mL) was added a solution of an equimolar amount of silver salts in acetone-d_6 (0.10 mL) at −78 °C in NMR tube. The NMR tube was shaken 10 times (white suspension of silver halide was formed immediately) and was kept until the upper layer became clear.

The NMR data for the cationic methyl and acyl complexes **2b** and **5** are as follows. The data for other series of **2** were already reported.[13a)]

[PdMe((CD$_3$)$_2$CO)(PMePh$_2$)$_2$]$^+$BF$_4^-$ 2b: ^{1}H NMR (acetone-d_6, −30 °C) δ=7.8—7.5 (20H, PMe(C_6H_5)$_2$, m), 2.18 (6H, P(CH_3)Ph$_2$, vt, J_{PH}=2.9 Hz), 0.65 (3H, PdCH_3, t, $^3J_{PH}$=6.6 Hz); ^{31}P{^{1}H} NMR (acetone-d_6, −30 °C) δ=13.6 (s); ^{13}C{^{1}H} NMR (acetone-d_6, −30 °C) δ=134.1 (vt, J_{PC}=6.7 Hz), 132.3, 130.3, 130.0 (Ph group), 10.4 (P(CH_3)Ph$_2$, vt, J_{PC}=14.1 Hz), −2.2 (PdCH_3).

[Pd(MeCO)((CD$_3$)$_2$CO)(PMe$_3$)$_2$]$^+$BF$_4^-$ 5: ^{1}H NMR (acetone-d_6, −30 °C) δ=2.51 (3H, PdCOCH_3, brs), 1.40 (18H, P(CH_3)$_3$, vt, J_{PH}=3.8 Hz); ^{31}P{^{1}H} NMR (acetone-d_6, −30 °C) δ=−19.2 ; ^{13}C{^{1}H} NMR (acetone-d_6, −30 °C) δ=226.4 (PdCOCH$_3$), 40.5 (PdCOCH$_3$, t, $^2J_{PC}$=17.9 Hz), 13.7 (P(CH_3)$_3$, vt, J_{PC}=14.1 Hz).

Observation of CO Insertion into the Complexes. Each organopalladium complex was dissolved in an appropriate solvent (0.45 mL) and CO gas was bubbled into the solution for 1 min at −78 °C. The solution was then vigorously shaken and subjected to NMR observation after 4 min.

Preparation of [PdMe(PMe$_3$)$_3$]$^+$BF$_4^-$ (6a).[34)] A solution of $AgBF_4$ (175 mg, 0.897 mmol) in acetone (2 mL) was added dropwise to an acetone (14 mL) solution of *trans*-[PdMe(Br)(PMe$_3$)$_2$] (317 mg, 0.897 mg) at −78 °C. After the pale yellow precipitate immediately formed was removed by filtration, 1 mol amt. of PMe_3 (0.079 mL, 0.905 mmol) was added at −60 °C. Stirring the solution for 2 h, followed by evaporation of the solvent, afforded the product, which was washed with Et_2O (3×3 mL) and hexane (3 mL) and dried in vacuo to give 259 mg (66%) of white powder. ^{1}H NMR (CD_2Cl_2, −30 °C) δ=1.49 (27H, P(CH_3)$_3$, s), 0.33 (3H, PdCH_3, d, $^3J_{PH}$=6.6 Hz); ^{31}P{^{1}H} NMR (CD_2Cl_2, −30 °C) δ=−14.1 (*cis* to Me, d, $^2J_{PP}$=41.1 Hz), −26.4 (*trans* to Me, t, $^2J_{PP}$=41.1 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2, −30 °C) δ=17.4 (P(CH_3)$_3$, d, J_{PC}=22.9 Hz), 14.9 (P(CH_3)$_3$, t, $^3J_{PC}$=14.8 Hz), 3.6 (PdCH_3, d, $^3J_{PC}$=88.8 Hz). Anal. Found: C, 27.56; H, 7.16%. Calcd for $C_{10}H_{30}BF_4P_3Pd$: C, 27.52; H, 6.93%.

Preparation of *trans*-[PdMe(Y)(PMe$_3$)$_2$]$^+$BF$_4^-$ (Y=Pyridine (6b), PhCH$_2$NC (6c), and ^{t}BuNC (6d)). A procedure similar to that for the preparation of [PdMe(PMe$_3$)$_3$]BF_4 was employed for preparation of **6b**, **6c**, and **6d** using pyridine, $PhCH_2NC$, or ^{t}BuNC, respectively.

6b: Yield 81%, white powder. ^{1}H NMR (acetone-d_6, −10 °C) δ=8.83 (2H, C_5H_5N, br), 8.08 (1H, C_5H_5N, br), 7.70 (2H, C_5H_5N, br), 1.24 (18H, P(CH_3)$_3$, vt, J_{PH}=3.5 Hz), 0.30 (3H, PdCH_3, t, J_{PH}=7.1 Hz); ^{31}P{^{1}H} NMR (acetone-d_6, −10 °C) δ=−14.0 (s); ^{13}C{^{1}H} NMR (acetone-d_6, −10 °C) δ=152.9, 140.4, 127.8 (pyridine), 13.0 (P(CH_3)$_3$, vt, J_{PC}=14.9 Hz), −8.0 (PdCH_3, t, J_{PC}=6.1 Hz). Anal. Found: C, 33.14; H, 6.04; N, 3.64%. Calcd for $C_{12}H_{26}BF_4NP_2Pd$: C, 32.79; H, 5.96; N, 3.19%.

6c: Yield 87%, brownish white powder. ^{1}H NMR (acetone-d_6, −30 °C) δ=7.6—7.4 (5H, CNCH$_2$C$_6$H$_5$, m), 5.22 (2H, CNCH_2C$_6$H$_5$, s), 1.52 (18H, P(CH_3)$_3$, vt, J_{PH}=3.3 Hz), 0.20 (3H, PdCH_3, t, $^3J_{PH}$=7.1 Hz); ^{31}P{^{1}H} NMR (acetone-d_6, −30 °C) δ=−11.9 (s); ^{13}C{^{1}H} NMR (acetone-d_6, −30 °C) δ=140.1 (CNCH$_2$C$_6$H$_5$), 133.4, 130.3, 130.2, 129.4 (Ph group), 48.6 (CNCH$_2$C$_6$H$_5$), 14.4 (P(CH_3)$_3$, vt, J_{PC}=15.6 Hz), −1.7 (PdCH_3). Anal. Found: C, 33.74; H, 5.85; N, 3.31%. Calcd for $C_{15}H_{28}BF_4NP_2Pd$: C, 37.73; H, 5.91; N, 2.93%.

6d: Yield 91%, white powder. ^{1}H NMR (CD_2Cl_2, −30 °C) δ=1.57 (9H, CNC(CH_3)$_3$, s), 1.51 (18H, P(CH_3)$_3$, vt, J_{PH}=3.5 Hz), 0.16 (3H, PdCH_3, t, $^3J_{PH}$=7.3 Hz); ^{31}P{^{1}H} NMR (CD_2Cl_2, −30 °C) δ=−13.6 (s); ^{13}C{^{1}H} NMR (CD_2Cl_2, −30 °C) δ=136.6 (CNC(CH$_3$)$_3$), 58.9 (CNC(CH$_3$)$_3$), 29.8 (CNC(CH$_3$)$_3$), 14.4 (P(CH_3)$_3$, vt, J_{PC}=6.1 Hz), −1.9 (PdCH_3). Anal. Found: C, 32.08; H, 6.67; N, 3.43%. Calcd for $C_{12}H_{30}BF_4NP_2Pd$: C, 32.50; H, 6.82; N, 3.16%.

Generation of *trans*-[PdMe(CNCH$_2$CO$_2$Me)(PMe$_3$)$_2$]$^+$BF$_4^-$ (6e) in NMR Tube. To a solution of [PdMe(Cl)(PMe$_3$)$_2$] (21.4 mg, 0.069 mmol) in acetone-d_6 (0.35 mL) was added a solution of 1 mol amt. of $AgBF_4$ (13.5 mg, 0.069 mmol) in acetone-d_6 (0.10 mL) at −78 °C in NMR tube. After the white powder (AgCl) was precipitated, methyl isocyanoacetate (6.3 μL, 0.069 mmol) was added. ^{1}H NMR (acetone-d_6, −30 °C) δ=5.04 (2H, CNCH_2CO$_2$Me, s), 3.79 (3H, CNCH$_2$CO$_2$CH_3, s), 1.58 (18H, P(CH_3)$_3$, vt, J_{PH}=3.5 Hz), 0.19 (3H, PdCH_3, t, $^3J_{PH}$=7.3 Hz); ^{31}P{^{1}H} NMR (acetone-d_6, −30 °C) δ=−11.4 (s); ^{13}C{^{1}H} NMR (acetone-d_6, −30 °C) δ=165.9 (CNCH$_2$CO$_2$Me), 142.5 (CNCH$_2$CO$_2$Me), 54.1 (CNCH$_2$CO$_2$Me), 46.8 (CNCH$_2$CO$_2$CH$_3$), 14.3 (P(CH_3)$_3$, vt, J_{PC}=16.1 Hz), −1.6 (PdCH_3, t, $^3J_{PC}$=4.7 Hz).

Generation of *trans*-[PdPh(CNCH$_2$Ph)(PMe$_3$)$_2$]$^+$BF$_4^-$ (6f) in NMR Tube. To a solution of [PdPh(Br)(PMe$_3$)$_2$] (22.6 mg, 0.054 mmol) in acetone-d_6 (0.35 mL) was added a solution of 1 mol amt. of $AgBF_4$ (10.5 mg, 0.054 mmol) in acetone-d_6 (0.10 mL) at −78 °C in NMR tube. After the pale yellow powder (AgBr) was precipitated, $PhCH_2NC$ (6.6 μL, 0.054 mmol) was added. ^{1}H NMR (acetone-d_6, −30 °C) δ=7.65—7.45 (5H, m), 7.30—6.95 (5H, m), 5.30 (2H, CNCH_2Ph, s), 1.28 (18H, P(CH_3)$_3$, vt, J_{PH}=3.7 Hz); ^{31}P{^{1}H} NMR (acetone-d_6, −30 °C) δ=−14.6 (s); ^{13}C{^{1}H} NMR (acetone-d_6, −30 °C) δ=166.6, 147.9 (t, $^2J_{PC}$=4.6 Hz), 144.2, 141.2, 141.1, 140.4, 140.3, 140.0, 135.9 (Ph groups), 59.6 (CNCH$_2$Ph), 25.2 (P(CH_3)$_3$, vt, J_{PC}=16.8 Hz).

Generation of *trans*-[Pd(MeC(O))(Y)(PMe$_3$)$_2$]$^+$BF$_4^-$ (Y= PMe$_3$ (7a), Pyridine (7b), PhCH$_2$NC (7c), and ^{t}BuNC (7d)). An acetone-d_6 or CD_2Cl_2 solution of [PdMe(Y)(PMe$_3$)$_2$]$^+$BF$_4^-$ in NMR tube was bubbled with CO (1 atm) gas, and the process of the reaction was followed by ^{1}H NMR. The identify of the complex produced was also confirmed by ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR.

7a: ^{1}H NMR (CD_2Cl_2, 22 °C) δ=2.46 (3H, PdCOCH_3, s), 1.47 (27H, P(CH_3)$_3$, m); ^{31}P{^{1}H} NMR (CD_2Cl_2, 22 °C) δ=−22.3 (*cis* to Me, d, $^2J_{PP}$=52.8 Hz), −31.2 (*trans* to Me, t, $^2J_{PP}$=52.8 Hz); ^{13}C{^{1}H} NMR (CD_2Cl_2, 22 °C) δ=246.9 (PdCOCH$_3$), 41.5 (PdCOCH$_3$, t, $^3J_{PC}$=17.6 Hz), 14.6, 13.1 (vt, J_{PC}=13.7 Hz).

7b: ^{1}H NMR (aceton-d_6, −30 °C) δ=8.85 (2H, C_5H_5N, br), 8.09 (1H, C_5H_5N, br), 7.70 (2H, C_5H_5N, br), 2.50 (3H, PdCOCH_3, s), 1.22 (18H, P(CH_3)$_3$, vt, J_{PH}=3.7 Hz); ^{31}P{^{1}H} NMR (acetone-d_6, −30 °C) δ=−19.4 (s); ^{13}C{^{1}H} NMR (acetone-d_6, −30 °C) δ=235.3 (PdCOCH$_3$), 152.5 (C_5H_5N), 140.5 (C_5H_5N), 127.6 (C_5H_5N), 41.5 (PdCOCH$_3$, t, $^3J_{PC}$=17.6 Hz), 13.05 (P(CH_3)$_3$, vt, J_{PC}=13.7 Hz).

7c: ^{1}H NMR (acetone-d_6, −10 °C) δ=7.6—7.4 (5H, CNCH$_2$C$_6$H$_5$, m), 5.22 (2H, CNCH_2C$_6$H$_5$, brs), 2.37 (3H, PdCOCH_3, s), 1.45 (18H, P(CH_3)$_3$, s); ^{31}P{^{1}H} NMR (acetone-d_6, −10 °C) δ=−17.7 (s); ^{13}C{^{1}H} NMR (acetone-d_6, −10 °C) δ=243.3 (PdCOCH$_3$), 149.8 (CNCH$_2$C$_6$H$_5$), 133.3, 130.3, 130.2, 129.3 (Ph group), 48.7 (CNCH$_2$C$_6$H$_5$), 42.0 (PdCOCH$_3$, t, $^3J_{PC}$=18.7 Hz), 15.1 (P(CH_3)$_3$, vt, J_{PC}=15.2 Hz).

7d: ^{1}H NMR (CD_2Cl_2, −30 °C) δ=2.35 (3H, PdCOCH_3, s),

1.55 (9H, CNC(CH_3)$_3$, s), 1.45 (18H, P(CH_3)$_3$, vt, J_{PH}=3.5 Hz); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −30 °C) δ=−20.2 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −30 °C) δ=242.9 (PdCOCH$_3$), 136.4 (CNC(CH$_3$)$_3$), 59.2 (CNC(CH$_3$)$_3$), 41.4 (PdCOCH$_3$, t, $^3J_{PC}$=18.6 Hz), 29.8 (CNC(CH_3)$_3$), 15.1 (P(CH_3)$_3$, vt, J_{PC}=14.9 Hz).

Preparation of *trans*-[PdMe(NO$_3$)(PMe$_3$)$_2$] (8). To an acetone (10 mL) solution of *trans*-[PdMe(Cl)(PMe$_3$)$_2$] (161 mg, 0.520 mmol) was added $AgNO_3$ (90 mg, 0.530 mmol) in 2 mL of water at 20 °C. A white suspension was formed immediately. The solution was stirred for 2 h and the silver chloride which formed was removed by filtration to give a clear solution. Evaporating the solution under reduced pressure gave the white solid, which was washed by cold ether (5 mL×2) and dried in vacuo: Yield 92% (161 mg), white powder. NMR and elemental analysis data for **8** have been already reported.[13b]

Generation of *trans*-[Pd(MeC(O))(NO$_3$)(PMe$_3$)$_2$] (9). An acetone-d_6 (0.4 mL) solution of *trans*-[PdMe(NO$_3$)(PMe$_3$)$_2$] (12.3 mg, 0.037 mmol) in NMR tube was bubbled with CO (1 atm) gas, and completion of the reaction was confirmed by ^{1}H NMR at −10 °C. The product was also characterized by $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR.

^{1}H NMR (acetone-d_6, −30 °C) δ=2.40 (3H, PdCOCH_3, s), 1.32 (18H, P(CH_3)$_3$, vt, J_{PH}=3.7 Hz); $^{31}P\{^1H\}$ NMR (acetone-d_6, −30 °C) δ=−17.5 (s); $^{13}C\{^1H\}$ NMR (acetone-d_6, −30 °C) δ=229.6 (PdCOCH$_3$), 41.2 (PdCOCH$_3$, t, $^3J_{PC}$=18.3 Hz), 13.6 (P(CH_3)$_3$, vt, J_{PC}=13.7 Hz); IR (KBr disk) 1681 cm^{-1} ($\nu_{C=O}$). Anal. Found: C, 26.59; H, 5.72; N, 3.70%. Calcd for $C_8H_{21}NO_4P_2Pd$: C, 26.42; H, 5.82; N, 3.85%.

Preparation of *trans*-[Pd(R(R′N)C)(X)(PMe$_3$)$_2$] (R=Me, R′=PhCH$_2$, X=Cl (10a); R=Me, R′=^{t}Bu, X=Cl (10b); R=Ph, R′=MeO$_2$CCH$_2$, X=Br (10c)). By using procedures analogous to those already reported,[24] *trans*-[Pd(Me(R′N)C)(Cl)(PMe$_3$)$_2$] was obtained from *trans*-[Pd(Me)(Cl)(PMe$_3$)$_2$] and RNC (1 mol amt).

10a: Yield 78%, white crystals. ^{1}H NMR (acetone-d_6, 22 °C) δ=7.5—7.2 (5H, PdC(NCH$_2$C$_6H_5$)CH$_3$, m), 4.88 (2H, PdC(NCH_2C$_6$H$_5$)CH$_3$, br), 2.26 (3H, PdC(NCH$_2$C$_6$H$_5$)CH_3, s), 1.35 (18H, vt, J_{PH}=3.7 Hz); $^{31}P\{^1H\}$ NMR (acetone-d_6, 22 °C) δ=−15.3; $^{13}C\{^1H\}$ NMR (acetone-d_6, 22 °C) δ=188.8 (PdC(NCH$_2$C$_6$H$_5$)CH$_3$, t, $^2J_{PC}$=6.2 Hz), 143.0, 129.4, 128.8, 127.4 (Ph group), 64.9 (PdC(NCH$_2$C$_6$H$_5$)CH$_3$), 33.8 (PdC(NCH$_2$C$_6$H$_5$)CH$_3$), 15.2 (P(CH_3)$_3$, vt, J_{PC}=14.4 Hz). Anal. Found: C, 42.19; H, 6.74; N, 3.59%. Calcd for $C_{15}H_{28}ClNP_2Pd$: C, 42.27; H. 6.62; N, 3.29%.

10b: Yield 82%, white powder. ^{1}H NMR (acetone-d_6, 22 °C) δ=2.16 (3H, PdC(NC(CH$_3$)$_3$)CH_3, s), 1.38 (27H, PdC(NC(CH_3)$_3$)CH$_3$ and P(CH_3)$_3$, m); $^{31}P\{^1H\}$ NMR (acetone-d_6, 22 °C) δ=−16.5 (s); $^{13}C\{^1H\}$ NMR (acetone-d_6, 22 °C) δ=175.4 (PdC(NC(CH$_3$)$_3$)CH$_3$, t, $^2J_{PC}$=6.8 Hz), 56.7 (PdC(NC(CH$_3$)$_3$)CH$_3$), 35.6 (PdC(NC(CH$_3$)$_3$)CH$_3$, t, $^4J_{PC}$=13.8 Hz), 15.2 (P(CH_3)$_3$, vt, J_{PC}=13.8 Hz). Anal. Found: C, 36.59; H, 7.60; N, 4.24%. Calcd for $C_{12}H_{30}ClNP_2Pd$: C, 36.75; H. 7.71; N, 3.57%.

10c: Yield 31%, pale yellow crystals. ^{1}H NMR (acetone-d_6, 22 °C) δ=8.25—8.15 (2H, C$_6H_5$, m), 7.45—7.35 (3H, C$_6H_5$, m), 4.82 (2H, PdC(NCH_2CO$_2$CH$_3$)C$_6$H$_5$, s), 3.74 (3H, PdC(NCH$_2$CO$_2$CH_3)C$_6$H$_5$, s), 1.34 (18H, P(CH_3)$_3$, vt, J_{PH}=3.7 Hz); $^{31}P\{^1H\}$ NMR (acetone-d_6, 22 °C) δ=−16.3 (s); $^{13}C\{^1H\}$ NMR (acetone-d_6, 22 °C) δ=257.3 (PdC(NCH$_2$CO$_2$CH$_3$)C$_6$H$_5$), 194.7 (PdC(NCH$_2$$CO_2CH_3$)C$_6H_5$, t, $^3J_{PC}$=5.3 Hz), 172.6, 145.1, 130.7, 129.3 (Ph group), 63.0 (PdC(NCH$_2$CO$_2$CH$_3$)C$_6$H$_5$, t, $^4J_{PC}$=6.5 Hz), 52.3 (PdC(NCH$_2$CO$_2$CH_3)C$_6$H$_5$), 15.4 (P(CH_3)$_3$, vt, J_{PC}=14.9 Hz). Anal. Found: C, 37.69; H, 5.52; N, 3.05%. Calcd for $C_{16}H_{28}BrNO_2P_2Pd$: C, 37.34; H. 5.48; N, 2.72%.

Generation of *trans*-[Pd(Me(R′N)C)(CNR′)(PMe$_3$)$_2$]$^+$BF$_4^-$ (R′=PhCH$_2$ (11a) and ^{t}Bu (11b)). To an acetone-d_6 or CD_2Cl_2 solution of [PdMe(CNR′)(PMe$_3$)$_2$]$^+$BF$_4^-$ in NMR tube was added R′NC (1 mol amt.), and the reaction was pursued by ^{1}H NMR. The product was also confirmed by $^{13}C\{^1H\}$ NMR.

11a: ^{1}H NMR (acetone-d_6, −30 °C) δ=7.6—7.2 (10H, Ph, m), 5.22 (2H, CNCH_2C$_6$H$_5$, s), 4.83 (2H, PdC(NCH_2C$_6$H$_5$)CH$_3$, s), 2.25 (3H, PdC(NCH$_2$C$_6$H$_5$)CH_3, s), 1.47 (18H, P(CH_3)$_3$, s); $^{31}P\{^1H\}$ NMR (acetone-d_6, −30 °C) δ=−11.9 (s); $^{13}C\{^1H\}$ NMR (acetone-d_6, −30 °C) δ=192.1 (PdC(NCH$_2$C$_6$H$_5$)CH$_3$), 140.1, 133.4, 130.3, 130.2, 129.5, 129.4, 128.6, 128.5, 127.6 (Ph groups), 64.4 (PdC(NCH$_2$C$_6$H$_5$)CH$_3$, t, $^4J_{PC}$=6.7 Hz), 48.8 (CNCH$_2$C$_6$H$_5$), 32.5 (PdC(NCH$_2$C$_6$H$_5$)CH$_3$, t, $^3J_{PC}$=9.8 Hz), 15.9 (P(CH_3)$_3$, vt, J_{PC}=15.8 Hz).

11b: ^{1}H NMR (CD_2Cl_2, −30 °C) δ=2.14 (3H, PdC(NC(CH$_3$)$_3$CH_3, s), 1.4—1.3 (27H, PdC(NC(CH_3)$_3$)CH$_3$ and P(CH_3)$_3$, m); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −30 °C) δ=−12.3 (s).

Generation of *trans*-[Pd(Me(PhCH$_2$N)C)(py)(PMe$_3$)$_2$]$^+$BF$_4^-$ (11c). To an acetone-d_6 (0.4 mL) solution of [PdMe(CNR′)(PMe$_3$)$_2$]$^+$BF$_4^-$ **6c** (32.6 mg, 0.073 mmol) in NMR tube was added pyridine (5.9 μL, 0.073 mmol), and the reaction product was characterized by ^{1}H NMR after 1 d. The product identity was also confirmed by $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR.

^{1}H NMR (acetone-d_6, −10 °C) δ=8.9—8.7 (2H, C$_5H_5$N, br), 8.1—7.9 (1H, C$_5H_5$N, br), 7.7—7.5 (2H, C$_5H_5$N, br), 7.49 (2H, *o*-Ph, d, $^3J_{HH}$=7.3 Hz), 7.30 (2H, *m*-Ph, dd, $^3J_{HH}$=7.3 and 7.0 Hz), 7.18 (1H, *p*-Ph, t, $^3J_{HH}$=7.0 Hz), 5.03 (2H, PdC(NCH_2Ph)CH$_3$, s), 2.35 (3H, PdC(NCH$_2$Ph)CH_3, s), 1.15 (18H, P(CH_3)$_3$, vt, J_{PH}=3.7 Hz); $^{31}P\{^1H\}$ NMR (acetone-d_6, −10 °C) δ=−17.9 (s); $^{13}C\{^1H\}$ NMR (acetone-d_6, 22 °C) δ=184.6 (PdC(NCH$_2$Ph)CH$_3$), 152.4, 142.6, 141.0, 130.5, 129.5, 128.8, 127.6 (Ph group and pyridine), 65.0 (PdC(NCH_2Ph)CH$_3$, t, $^4J_{PC}$=6.1 Hz), 32.6 (PdC(NCH$_2$Ph)CH_3, t, $^3J_{PC}$=9.2 Hz), 14.5 (P(CH_3)$_3$, vt, J_{PC}=14.5 Hz).

Generation of *trans*-[Pd(Me(PhCH$_2$N)C)(acetone)(PMe$_3$)$_2$]$^+$BF$_4^-$ (12) by Treatment of *trans*-[Pd(Me(PhCH$_2$N)C)(Cl)(PMe$_3$)$_2$] (10) with 1 mol amt. of AgBF$_4$. The same procedure used for the generation of the cationic complexes [PdMe(s)(L)$_2$]$^+$BF$_4^-$ from the neutral complexes [PdMe(X)(L)$_2$] **1** was applied to produce **12**.

^{1}H NMR (acetone-d_6, −30 °C) δ=7.5—7.3 (5H, Ph, m), 4.84 (2H, PdC(NCH_2Ph)CH$_3$, br), 2.17 (3H, PdC(NCH$_2$Ph)CH_3, s), 1.44 (18H, P(CH_3)$_3$, vt, J_{PH}=3.5 Hz); $^{31}P\{^1H\}$ NMR (acetone-d_6, −30 °C) δ=−13.2 (s); $^{13}C\{^1H\}$ NMR (acetone-d_6, −30 °C) δ=191.9 (PdC(NCH$_2$Ph)CH$_3$, t, $^2J_{PC}$=6.2 Hz), 141.3, 130.5, 129.9, 129.5 (Ph group), 65.8 (PdC(NCH$_2$Ph)CH$_3$) 37.5 (PdC(NCH$_2$Ph)CH$_3$), 14.3 (P(CH_3)$_3$, vt, J_{PC}=15.3 Hz).

Reaction of *trans*-[Pd(Me(PhCH$_2$N)C)(acetone)(PMe$_3$)$_2$]$^+$BF$_4^-$ (12) with CO to Generate *trans*-[Pd(Me(PhCH$_2$N)CC(O))(CO)(PMe$_3$)$_2$]$^+$BF$_4^-$ (13). After the generation of *trans*-[Pd(Me(PhCH$_2$N)C)(acetone)(PMe$_3$)$_2$]$^+$BF$_4^-$ in NMR tube by treatment of *trans*-[Pd(Me(PhCH$_2$N)C)(Cl)(PMe$_3$)$_2$] (24.3 mg, 0.057 mmol) with $AgBF_4$ (11.2 mg, 0.058 mmol) in acetone-d_6, CO (1 atm) was bubbled at −30 °C. The reaction mixture was stored at −30 °C for 18 d. The product was confirmed by ^{1}H and $^{13}C\{^1H\}$ NMR but no coordinating-CO was observed. ^{1}H NMR (acetone-d_6, −30 °C) δ=7.5—7.3 (5H, Ph, m), 4.84 (2H, PdC(O)C(NCH_2Ph)CH$_3$, br), 2.17 (3H, PdC(O)C(NCH$_2$Ph)CH_3, s), 1.44 (18H, P(CH_3)$_3$, vt, J_{PH}=3.5 Hz); $^{13}C\{^1H\}$ NMR (acetone-d_6, −30 °C) δ=235.64 (PdC(O)C(NCH$_2$Ph)CH$_3$), 192.0 (PdC(O)C(NCH$_2$Ph)CH$_3$, t, $^2J_{PC}$=6.2 Hz), 136.4, 130.3, 129.7, 118.3 (Ph group), 60.3 (PdC(O)C(NCH_2Ph)CH$_3$), 34.5 (PdC(O)C(NCH$_2$Ph)CH_3), 13.5 (P(CH_3)$_3$, vt, J_{PC}=15.3 Hz).

Generation of [Pd(MeC(O)(PhCH$_2$N)C)(CNCH$_2$Ph)-(PMe$_3$)$_2$] (14). After the generation of *trans*-[Pd(MeC(O))-(CNCH$_2$Ph)(PMe$_3$)$_2$] in NMR tube by treatment of *trans*-[Pd(Me)-(CNCH$_2$Ph)(PMe$_3$)$_2$] (25.9 mg, 0.054 mmol) with CO (1 atm) in acetone-d_6, PhCH$_2$NC (6.6 μL, 0.054 mmol) was added at −20 °C. The reaction mixture was stored at −20 °C for 3 weeks. The insertion of PhCH$_2$NC into acetyl–palladium bond was confirmed by NMR. ^{1}H NMR (acetone-d_6, −30 °C) δ=7.6—7.3 (10H, Ph, m), 5.4—4.8 (4H, CNC*H*$_2$Ph, br), 2.37 (3H, C(O)C*H*$_3$, s), 1.48 (18H, P(C*H*$_3$)$_3$, s); ^{13}C{^{1}H} NMR (acetone-d_6, −30 °C) δ=243.0 (PdC(NCH$_2$Ph)*C*(O)CH$_3$), 185.3 (Pd*C*(NCH$_2$Ph)C(O)CH$_3$), 140.3, 134.0 (br), 130.3, 130.2, 129.8, 129.4, 128.6, 128.5, 127.8 (Ph groups), 47.0 (CN*C*H$_2$Ph, br), 42.0 (CN*C*H$_2$Ph), 15.3 (P(*C*H$_3$)$_3$, br).

Preparation of [PdMe$_2$(bpy)] (15a).[36] A suspension of [PdCl$_2$(bpy)] (3.00 g, 9.00 mmol) in THF (30 mL) was cooled to −78 °C, and a hexane solution of MeLi (30 mL, 22.8 mmol) was added. The mixture was stirred at −30—0 °C for 4 h and then hydrolyzed with water. The crude product isolated from the organic layer by evaporation was washed by ether (10 mL×2) and dried under vacuum. The residue was dissolved in hot acetone and passed through a short active carbon column, and a yellow powder (2.282 g, 7.80 mmol) was obtained after evaporation. Yield 87%. ^{1}H NMR (acetone-d_6, 22 °C) δ=8.76 (2H, d, $^2J_{HH}$=5.0 Hz), 8.44 (2H, d, $^2J_{HH}$=8.3 Hz), 8.15 (2H, d, $^2J_{HH}$=8.3, 7.6 Hz), 7.67 (2H, d, $^2J_{HH}$=7.6, 5.0 Hz), 0.23 (6H, PdC*H*$_3$, s); ^{13}C{^{1}H} NMR (acetone-d_6, 22 °C) δ=156.3, 149.0, 139.3, 127.5, 123.6 (bpy), −6.0 (Pd*C*H$_3$).

Preparation of [PdMe(dmf)(bpy)]BF$_4$ (16). A solution of [PdMe$_2$(bpy)] (517 g, 1.77 mmol) in DMF (300 mL) was cooled to −78 °C, and HBF$_4$·OMe$_2$ (215 μL, 1.77 mmol) was added. After stirring the solution at −40—0 °C for 2 h, the solution was evaporated in vacuo to give the brown solid, which was washed by cold acetone (2 mL) and ether (2 mL×2) and dried in vacuo. Yield 48% (247 mg, 0.565 mmol). ^{1}H NMR (DMF-d_7, −30 °C) δ=8.7—7.7 (8H, m), 0.82 (3H, PdC*H*$_3$, s); ^{13}C{^{1}H} NMR (DMF-d_7, −30 °C) δ=157.9, 153.4, 151.4, 151.3, 148.1, 141.2, 128.2, 125.5, 125.0, 123.7 (bpy), 4.3 (Pd*C*H$_3$). Anal. Found: C, 38.20; H, 3.91; N, 9.66%. Calcd for C$_{14}$H$_{18}$BF$_4$N$_3$OPd: C, 38.43; H, 4.15; N, 9.60%.

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