Removal of a Palladium-Bound Tertiary Phosphine Ligand with Silver(I) Salts to Generate Cationic Monoorganopalladium(II) Complexes Having One Trimethylphosphine Ligand

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Treatment of neutral monoorganobis(trimethylphosphine)palladium(II) halide complexes, *trans*-[PdR(X)(L)$_2$] **1** (R = Me, Et, or Ph group, X = halide ligand, L = trimethylphosphine), with an equimolar amount of a silver salt such as $AgBF_4$ usually gives cationic monoorganobis(trimethylphosphine) palladium(II) complexes, *trans*-[PdR(s)L$_2$]BF_4 (s = solvent) **2**. But employment of an excess amount of the silver salt in the reaction with **1** or treatment of **2** with an additional amount of the silver salt yields a cationic monoorganopalladium(II) complex coordinated with one PMe_3 ligand, *cis*-[PdR(L)(s)$_2$]$^+$ **3** by removing one of the PMe_3 ligands in **2**. The cationic mono-phosphine complex **3** can be also prepared by addition of an equimolar amount of a silver salt to the neutral dinuclear Cl-bridged, monophosphine complex [PdMe(μ-Cl)(PMe_3)]$_2$ **5**. The *cis* configuration of **3** was supported by comparison of the NMR spectra with those of cationic, cyclooctadiene (COD)-coordinated monomethylmono(trimethylphosphine)palladium complex, *cis*-[PdMe(PMe_3)(cod)]BF_4, **6**. Complex **6** was prepared by two routes, by treatment of **3** with COD and by reaction of [PdMe(Cl)(cod)] **7** with an equimolar amount of $AgBF_4$ followed by addition of an equimolar amount of PMe_3. The cationic mono-phosphine complex **3** having one PMe_3 ligand shows greater reactivity for the CO insertion than the bis-phosphine complex **2**.

Organotransition metal complexes play essential roles in various transition metal-catalyzed processes such as olefin arylation, polymerization, and carbonylation.[1] In some of these reactions, enhancement of the reactivity of neutral organometallic complexes of early as well as late transition metals toward unsaturated compounds such as olefins and carbon monoxide has been recognized by generating cationic organotransition metal complexes.[2—4] For palladium-catalyzed processes such as olefination of aryl halides, which are considered to proceed through an intermediate organopalladium halide complex, marked rate acceleration effects are observed by addition of silver salts.[5] The rate enhancement is considered to be caused by removal of the halide ligand from the intermediate arylpalladium halide complex with the silver salt. In the previous papers[3,6—8] we have established that the principal reason for the rate acceleration by converting the neutral monoorganobis(tertiary phosphine)-palladium halide complexes **1** to the cationic monoorganobis-(phosphine)palladium complexes **2** is the generation of an available coordination site for the incoming substrate at a position *cis* to the alkyl or aryl ligand.

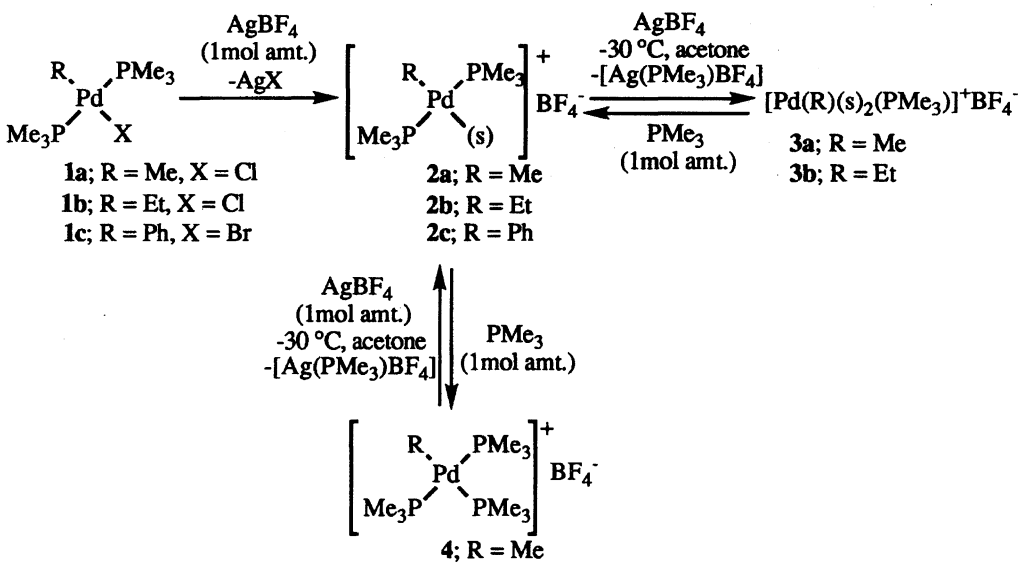
In the course of our study to clarify the effect of addition of silver salts to the organopalladium halide complexes, we found that use of an excess amount of the silver salt gives a new complex by stripping one of the two PMe_3 ligands. Although some examples of neutral monoorganopalladium complexes having one tertiary phosphine ligand per palladium have been reported,[9—12] the properties of *cationic* monoorganopalladium complexes with one tertiary phosphine ligand have not been clarified. We wish to report here the characterization of the novel cationic monoorganopalladium complexes having one PMe_3 ligand and their reactivities toward CO.

Results and Discussion

Reactions of [PdR(X)(PMe_3)$_2$] (R=Me, Et and Ph, X=Cl and Br) 1 with $AgBF_4$. As previously reported,[7,8] treatment of the neutral monoorganopalladium halide complexes *trans*-[PdR(X)(PMe_3)$_2$] **1** with an equimolar amount of $AgBF_4$ in acetone at -30 °C yields cationic complexes [PdR(s)(PMe_3)$_2$]$^+BF_4^-$ (R = Me and Et; s = acetone) **2** as shown in Scheme 1.

The *trans* configuration of the bis-phosphine complex **2** can be readily established by NMR; the ^{1}H and the ^{13}C NMR of the coordinated PMe_3 ligands show the virtual triplet patterns,[13] the ^{31}P NMR giving a singlet and the palladium-bonded carbon showing the triplet by coupling with the two mutually *trans* situated PMe_3 ligands.

Treatment of **1** with an excess amount of $AgBF_4$, or further treatment of the bis-phosphine complex **2** with 2.4 molar amounts of the silver salt caused further changes of the spectra (Tables 1 and 2). The virtual triplet of the coordinated PMe_3 ligands in the ^{1}H NMR of **2a** was displaced by a doublet (1.48 ppm, J_{PH} = 11.7 Hz) accompanied by appearance of another doublet (1.45 ppm, J_{PH} = 8.4 Hz), which was ascribed to the adduct of PMe_3–$AgBF_4$ by comparison with the spec-



Scheme 1.

Table 1. ^{1}H NMR Data (−30 ° C, acetone-d_6) (ppm)

Run	Preparative method	Complex obtained	P(CH_3)$_3$	CH_3	$-CH_2-$
1	**1a** + $AgBF_4$ (1.0 equiv)	(**2a**)	1.36 (vt, J_{PH} = 3.3 Hz)	0.49 (t, $^3J_{PH}$ = 7.1 Hz)	
2	**1b** + $AgBF_4$ (1.0 equiv)	(**2b**)	1.38 (vt, J_{PH} = 3.3 Hz)	1.03 (tt, $^4J_{PH}$ = 4.0 Hz $^3J_{HH}$ = 8.0 Hz)	1.43—1.63 (m)
3	**1a** + $AgBF_4$ (4.7 equiv)	(**3a**)[a]	1.47 (d, $^2J_{PH}$ = 11.4 Hz)	0.52 (d, $^3J_{PH}$ = 1.1 Hz)	
4	**1b** + $AgBF_4$ (3.4 equiv)	(**3b**)[a]	1.48 (d, $^2J_{PH}$ = 11.7 Hz)	0.87 (dt, $^4J_{PH}$ = 6.6 Hz $^3J_{HH}$ = 7.3 Hz)	1.56 (dq, $^4J_{PH}$ = 4.0 Hz $^3J_{HH}$ = 7.3 Hz)
5[b]	**5** + $AgBF_4$ (1.0 equiv)	(**3a**)	1.49 (d, $^2J_{PH}$ = 11.7 Hz)	0.55 (d, $^3J_{PH}$ = 1.1 Hz)	

a) In addition to the signals arising from **3a** or **3b** a doublet (1.45 ppm, $^2J_{PH}$ = 8.4 Hz) ascribed to the PMe_3·$AgBF_4$ adduct was observed at −30 °C. b) Acetone-d_6 and CD_2Cl_2 (4 : 1) solution.

Table 2. ^{31}P NMR Data (−30 ° C, acetone-d_6)

Run	Preparative method	Complex obtained[1]	Chemical shift (ppm)
1	**1a** + $AgBF_4$ (1.0 equiv)	(**2a**)	−13.2
2	**1b** + $AgBF_4$ (1.0 equiv)	(**2b**)	−14.3
3[a]	**1a** + $AgBF_4$ (4.7 equiv)	(**3a**)	4.5
4[a]	**1b** + $AgBF_4$ (3.4 equiv)	(**3b**)	2.0
5	**5** + $AgBF_4$ (1.0 equiv)	(**3a**)	3.9

a) In addition to the signals arising form **3a** or **3b** a singlet (−35.7 ppm) ascribed to the PMe_3 ·$AgBF_4$ adduct was observed at −30 °C.

trum of the separately prepared equimolar mixture of PMe_3 and $AgBF_4$ in acetone without the palladium complex.[14] The result indicates that one of the two PMe_3 ligands in complex **2** was stripped away by action of the silver salt to yield monophosphine complexes **3** (see Scheme 1). Further abstraction of the PMe_3 ligand by addition of silver salt to **3a** and **3b** was not observed. The cationic complexes **3** were too thermally unstable to be isolated and were not amenable to elemental analysis. Addition of an equimolar amount of PMe_3 to **3** restored the bis-phosphine complexes **2**. A change similar to the behavior of the methylpalladium complex **1a** was observed with the ethylpalladium complex **1b**, as shown in Tables 1 and 2. On the other hand, the phenylpalladium bisphosphine complex **2c** was found to be reluctant to lose the PMe_3 ligand; addition of 9 molar amounts of $AgBF_4$ to **2c** removed only 45% of the PMe_3 ligand from the palladium complex at −30 °C in acetone-d_6, as revealed by ^{1}H NMR.

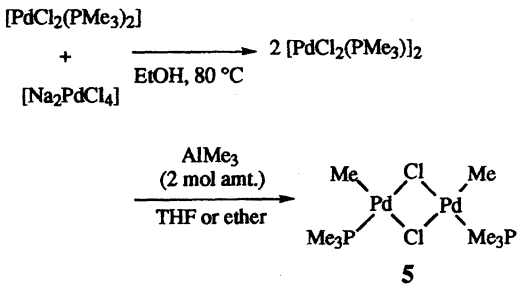
Similar phosphine abstraction was observed by using other silver salts such as $AgPF_6$ and AgOTf with formation of the corresponding cationic monomethylpalladium complexes having different anions. The ^{1}H, ^{13}C, and ^{31}P NMR spectra of these complexes were identical with those of the

complexes having the BF_4 counter anion. The results suggest the absence of direct interaction of the counter anions with the cationic palladium center. The previously reported cationic monomethylpalladium complexes having bidentate phosphine ligands, $[PdMe(s)(dmpe)]^+BF_4^-$ and $[PdMe(s)(dppe)]^+BF_4^-$ (dmpe=1,2-bis(dimethylphosphino)ethane and dppe=1,2-bis(diphenylphosphino)ethane), did not show any sign of interaction of the coordinated phosphine ligands with excess silver salts and no removals of the chelating tertiary phosphines by silver salts were observed.

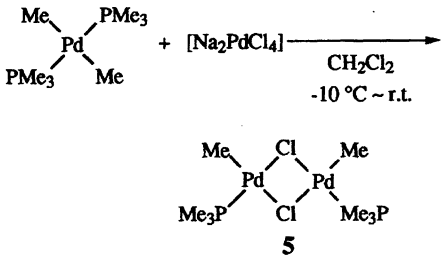
As reported in the previous paper,[7a,8] addition of an equimolar amount of PMe_3 to the bis-phosphine complex **2a** gives the tris-phosphine complex $[PdMe(PMe_3)_3]^+BF_4^-$ **4**. Conversely, addition of an equimolar amount of $AgBF_4$ at -30 °C in acetone to **4** was found to abstract the PMe_3 ligand *trans* to the methyl ligand in the tris-phosphine complex to regenerate the bis-phosphine complex **2a** (Scheme 1).

Generation of Cationic Methylmono(phosphine)-palladium Complex from Dimeric Methyl(*μ*-chloro)-mono(phosphine)palladium Complex. Although the NMR spectra of **3** support the formation of a methylpalladium complex coordinated with one PMe_3 ligand and solvent molecules, the NMR spectra do not reveal its configuration, whether it is *cis* or *trans*. The instability of the complex precluded its isolation. Thus we attempted to characterize it by comparison with the NMR spectra of a cationic methylpalladium complex having one PMe_3 ligand that is forced to occupy the site *cis* to the Pd–Me by another chelating ligand spanning the remaining mutually *cis* positions.

For this purpose we prepared first the neutral dimeric chloride-bridged methylpalladium complex having one PMe_3 ligand per palladium, **5**, through two routes. One route involves the initial preparation of a neutral dimeric palladium chloride coordinated with one PMe_3 per palladium by the reaction of $[PdCl_2(PMe_3)_2]$ with $[Na_2PdCl_4]$ in ethanol at 80 °C, followed by methylation with $AlMe_3$ (Eq. 1).[10] The other route involves the reaction of $[PdMe_2(PMe_3)_2]$ with an equimolar amount of $[Na_2PdCl_4]$ in CH_2Cl_2 (Eq. 2). Both routes gave the identical neutral chloride-bridged methylpalladium complex dimer having one PMe_3/Pd, **5**. The NMR spectra of **5** suggest the formation of a sole product with a "*cis*" configuration, as shown in Eqs. 1 and 2.[9b]



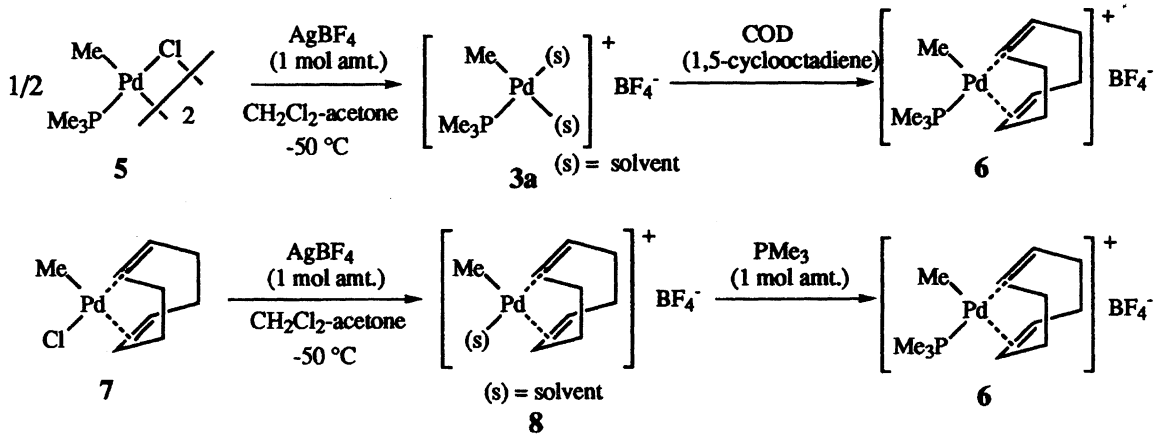
(1)



(2)

Addition of two molar amounts of $AgBF_4$ (an equimolar amount/Pd) to the dimeric, chloride-bridged neutral complex **5** in acetone-d_6 at -30 °C afforded the corresponding cationic complex **3a** showing the identical NMR spectra with those prepared by treatment of **1a** with 3.4 molar amounts of $AgBF_4$ (Scheme 1). The cationic complex **3a** treated with an equimolar amount of COD (1,5-cyclooctadiene) gave $[PdMe(PMe_3)(cod)]^+BF_4^-$ **6**, which is stable at room temperature and could be isolated as an analytically pure complex. The COD-coordinated complex **6** was also prepared by addition of PMe_3 to $[PdMe(s)(cod)]^+BF_4^-$ **8**, which was in turn generated by removal of the halide ligand in [PdMe(Cl)(cod)] **7** with $AgBF_4$ in situ (Scheme 2).

Since complex **6** has a chelating COD ligand, the disposition of the palladium-bonded methyl ligand and the PMe_3 ligand in **6** is considered to be cis, which is indicated by NMR results showing the small coupling constant of the doublet methyl signal ($^3J_{PH}$=3.3 Hz). The still smaller $^3J_{PH}$ value



Scheme 2.

of 1.1 Hz of the doublet methyl signal in **3a** suggests the *cis* configuration for complex **3** without the COD ligand.[15]

Comparison of the Reactivities of the Cationic Bis(trimethylphosphine) Complex 2a and Mono(trimethylphosphine) Complex 3a toward CO Insertion. We have previously reported that the cationic, solvent-coordinated *cis* monomethylpalladium complexes having the chelate phosphine ligands such as DPPE and DMPE and a coordination site available adjacent to the methyl ligand showed higher reactivity for the incoming CO than the *trans* bis-phosphine complex such as **2a** having two PMe_3 ligands. In order to examine the influence of the site and the number of the phosphine coordination on the CO insertion, the reactivity of the cationic mono-phosphine complex **3a** was compared with that of the cationic bis-phosphine complex **2a**. The CO insertion into **2a** and **3a** to give the acetylpalladium complexes followed the first order kinetics in the concentration of **2a** and **3a** over 50% conversion. Comparison of the rate constants for the CO insertion into **2a** and **3a** under identical conditions at −20 °C in acetone-d_6 under atmospheric pressure of CO showed that the CO insertion rate into the cationic mono-phosphine complex **3a** was about four times greater than that for the bis-phosphine complex **2a**. The increase in the reactivity of the cationic methylpalladium complex by removing one of the two PMe_3 ligands in **2a** suggests that creation of a coordination site *cis* to the methyl ligand is important to facilitate the migratory insertion of CO into the methylpalladium complex.[16]

Treatment of the cationic methylpalladium complex **8** having no phosphine ligands with CO led to decomposition with dissociation of the COD ligand.

We next examined the reactions of the neutral and the cationic mono(methyl)mono(phosphine) palladium complexes **3a**, **6**, and **8** with methyl acrylate and styrene by means of ^{1}H NMR, but the methylmono(phosphine)palladium complexes prepared in the present study as well as methylbis(phosphine)palladium complex **2a** proved unreactive toward olefins.

Conclusion

The present study revealed that a silver salt has the ability not only to generate a cationic organopalladium complex from a neutral organopalladium halide complex by halide removal, but also is capable of abstracting further the coordinated tertiary phosphine ligand. To our knowledge, this is the first report of the removal of the coordinated tertiary phosphine ligand by a silver salt from an organopalladium complex and of the characterization of the cationic mono-phosphine-coordinated organopalladium complex that shows greater reactivity than the bis-phosphine complex.[17,18] The results may be relevant to the palladium-catalyzed synthetic procedures using a silver salt as an accelerator of the reaction.

Experimental

General Procedures. All the manipulations were performed under argon atmosphere by using Schlenk techniques. $[PdMe(Cl)(PMe_3)_2]$,[8] $[PdEt(Cl)(PMe_3)_2]$,[19] $[PdPh(Br)(PMe_3)_2]$,[8] $[PbMe(Cl)(dmpe)]$,[8] $[PdMe(Cl)(dppe)]$,[20] $[PdMe(PMe_3)_3]^+BF_4^-$,[8] *trans*-$[PdMe_2(PMe_3)_2]$,[21] and $[PdMe(Cl)(cod)]$[22] were synthesized by literature methods. $[PdCl_2(PMe_3)]_2$ was prepared by treatment of $[Na_2PdCl_4]$ with $[PdCl_2(PMe_3)_2]$ in ethanol according to the literature method.[23] All the tertiary 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), $^{13}C\{^1H\}$ (67.9 MHz, referenced to $SiMe_4$ via the solvent resonance), and $^{31}P\{^1H\}$ (109.4 MHz, referenced to 85% H_3PO_4 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.

Treatment of $[PdR(Cl)(PMe_3)_2]$ (R=Me and Et) (1), $[PdMe(PMe_3)_3]^+BF_4^-$ (4), or $[PdMe(Cl)(PMe_3)]_2$ (5), [PdMe(Cl)(cod)] (7) with $AgBF_4$ in NMR tube. To a solution containing the complexes **1**, **4**, **5**, or **7** in acetone-d_6 (0.35 mL) was added a solution of an equimolar amount or an excess amount of silver salts dissolved 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 ethyl complexes **2** and **3** are as shown in Tables 1 and 2. The NMR data for $[PdMe(acetone)(cod)]^+BF_4^-$ **8** are as follows. ^{1}H NMR (acetone-d_6, −30 °C) δ=5.8 (2H, COD, m), 5.4 (2H, COD, m), 2.7 (4H, COD, m), 2.5 (4H, COD, m,), 1.09 (3H, PdCH_3, s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −30 °C) δ=124.4 (COD), 101.4 (COD), 30.9 (COD), 27.5 (COD), 14.4 (PdCH_3, s).

Kinetic Studies of CO Insertion into the Methylpalladium Complexes. To a solution containing the neutral methylpalladium complex **1a** (6.0×10^{-3} mmol) in acetone-d_6 (0.35 mL) was added a solution of an equimolar amount or an excess amount of $AgBF_4$ dissolved in acetone-d_6 (0.10 mL) at −78 °C in an NMR tube. CO gas was bubbled into the solution for 1 min at −78 °C. The solution (1.3×10^{-2} mol dm^{-3}) was then vigorously shaken and subjected to ^{1}H NMR observation after 4 min. The amounts of acetyl complexes were determined by measuring the intensities of Pd–C(O)CH_3 signals at 2.53 ppm after suitable time intervals at −20 °C. The NMR data for *trans*-$[Pd\{CH_3C(O)\}(CO)(PMe_3)_2]^+BF_4^-$ generated from bis(trimethylphosphine)complex **2a** under CO have been already reported.[7a] The structure of the product obtained by treatment of CO with mono(trimethylphosphine)complex **3a** was not fully confirmed. ^{1}H NMR (acetone-d_6, −20 °C) δ=2.53 (3H, PdC(O)CH_3, s), 1.50 (9H, P(CH_3)$_3$, d, J_{PH}=12.5 Hz).

Observation of (Trimethylphosphine)silver(I) Species. To a solution containing $AgBF_4$ (32.0 mg, 0.164 mmol) in acetone-d_6 (0.45 ml) was added PMe_3 (17 μL, 0.164 mmol) at −30 °C. The formation of $PMe_3\cdot AgBF_4$ complex was confirmed by ^{1}H and ^{31}P NMR at −30 °C (see Tables 1 and 2).

Preparation of $[PdMe(Cl)(PMe_3)]_2$ (5) from $[PdCl_2(PMe_3)]_2$ with $AlMe_3$. The same procedure[10] used for the preparation of $[PdMe(Cl)(L)]_2$ (L=phosphine ligands) was employed for the preparation of **5**. Yield: 589 mg (63%) as a white powder. ^{1}H NMR (CD_2Cl_2, −30 °C) δ=1.44 (18H, P(CH_3)$_3$, d, $^2J_{PH}$=11.0 Hz), 0.59 (6H, PdCH_3, br); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −30 °C) δ=−1.05 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −30 °C) δ=15.4 (P(CH_3)$_3$, d, J_{PC}=35.0 Hz), 0.25 (PdCH_3, s). Found: C, 20.98; H, 5.16%. Calcd for $C_8H_{24}Cl_2P_2Pd_2$: C, 20.62; H, 5.19%.

Preparation of $[PdMe(Cl)(PMe_3)]_2$ (5) from $[PdMe_2(PMe_3)_2]$ and $[Na_2PdCl_4]$. A CH_2Cl_2 (30 mL) solution containing *trans*-

$[PdMe_2(PM_3)_2]$ (418 mg, 1.45 mmol) was added to $[Na_2PdCl_4]$ (426 mg, 1.45 mmol) at −10 °C. When the mixture was stirred for 15 h while increasing the temperature gradually to 20 °C, the color of the suspension changed from brown to black. The insoluble particles formed were removed by filtration to give a clear yellow solution, which was concentrated to dryness. A pale-yellow solid obtained was washed with THF (1 mL×3) and hexane (2 mL) and dried in vacuo to yield a white solid. Yield: 190 mg (22%). The NMR spectrum showed identical resonances with the sample prepared by the procedure described above.

Preparation of $[PdMe(PMe_3)(cod)]^+BF_4^-$ (6). Method A: A solution containing $AgBF_4$ (243 mg, 1.25 mmol) in acetone (2 mL) was added dropwise to a CH_2Cl_2 (10 mL) solution of [PdMe(Cl)(cod)] (333 mg, 1.28 mg) at −50 °C. A white suspension which immediately formed was stirred for 3 h at −50 °C, and silver chloride was removed by filtration to afford a clear solution. Trimethylphosphine (130 μL, 1.26 mmol) was added with a syringe to the solution at −30 °C. The solution was stirred for 1 h and the solvent was removed by evaporation to afford a white powder, which was washed with hexane (3 mL×2) and dried in vacuo. Yield: 259 mg (90%). ^{1}H NMR (acetone-d_6, −30 °C) δ=6.1 (4H, COD, m), 2.8 (4H, COD, m), 2.5 (4H, COD, m), 1.68 (9H, $P(CH_3)_3$, d, J_{PH}=11.4 Hz), 0.92 (3H, $PdCH_3$, d, $^3J_{PH}$=3.3 Hz); $^{31}P\{^1H\}$ NMR (acetone-d_6, −30 °C) δ=−3.4; $^{13}C\{^1H\}$ NMR (acetone-d_6, −30 °C) δ=123.2 (COD), 119.6 (COD), 31.8 (COD), 28.9 (COD), 13.9 ($P(CH_3)_3$, d, J_{PC}=33.7 Hz), 9.0 ($PdCH_3$, s). Found: C, 37.03; H, 6.06%. Calcd for $C_{12}H_{24}BF_4PPd$: C, 36.72; H, 6.16%.

Method B: To a CH_2Cl_2 (8 mL) solution containing $[PdMe(Cl)(PMe_3)]_2$ **5** (189 mg, 0.405 mmol) was added $AgBF_4$ (158 mg, 0.809 mmol) in 1 mL of acetone at −50 °C. A white suspension was immediately formed and the mixture was stirred for 2 h at −50—−20 °C. The silver chloride was removed by filtration to give a clear solution to which COD (0.1 mL, 0.815 mmol) was added dropwise. After further stirring for 1 h at −20 °C, the solution was dried in vacuo to afford a white powder. The white powder was washed with hexane (3 mL×2) and dried in vacuo again. Yield: 142 mg (41%). The product was characterized as $[PdMe(PMe_3)(cod)]^+BF_4^-$ **6** by comparison with the NMR spectra of **6** obtained by the method A.

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