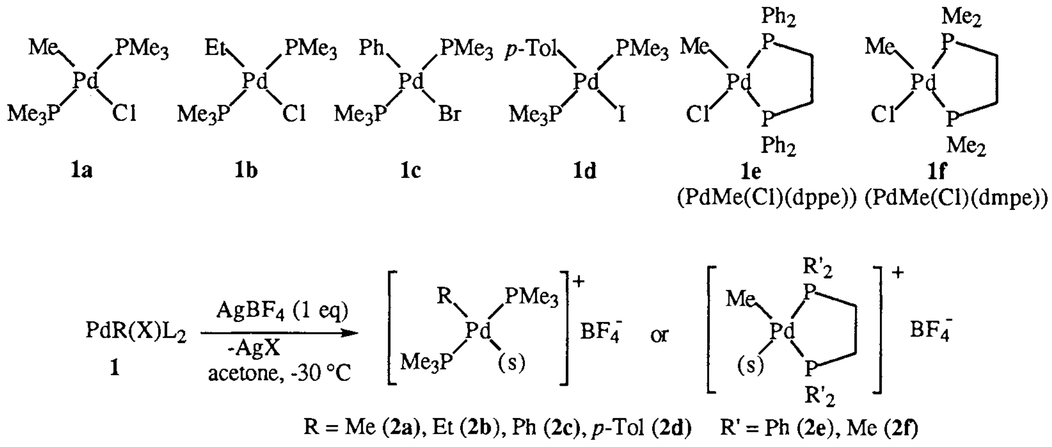
CHEMISTRY LETTERS, pp. 2171-2174, 1994.

# Remarkable Rate Enhancement in CO Insertion into Pd-C Bond by Generating Cationic Organopalladium Complexes $[PdR(s)L_2]^+BF_4^-$ (R = Alkyl Group, s = Acetone, L = Phosphine Ligands) from Neutral Monoorganopalladium Complexes $[PdR(X)L_2]$ (X = Halide)

Yoshihito KAYAKI, Futoshi KAWATAKA, Isao SHIMIZU, and Akio YAMAMOTO*
Department of Applied Chemistry, School of Science and Engineering,
Waseda University, 3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169

Removal of the halide ligand X in $PdR(X)L_2$ with $AgBF_4$ generates solvent-coordinated cationic organopalladium complexes $[PdR(s)L_2]BF_4$ which show much higher reactivities for CO insertion than the parent neutral complexes.

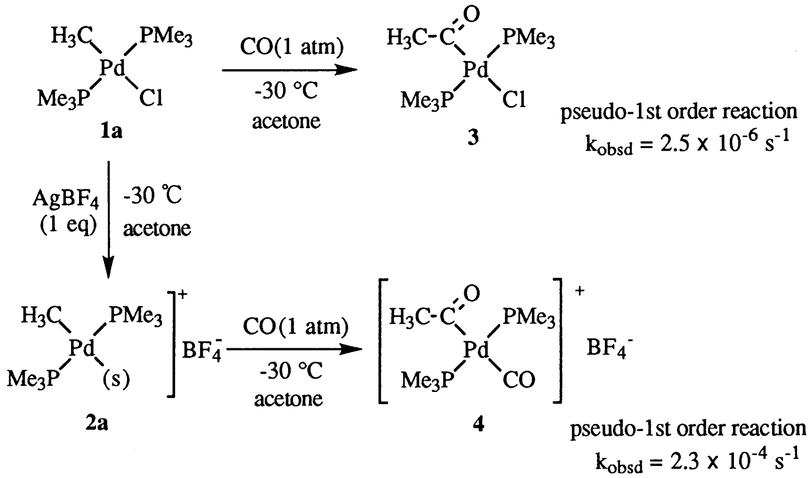
Clarification of elementary processes involving organopalladium complexes is essential to understand mechanisms of palladium-catalyzed reactions such as olefin arylation and carbonylation processes (Heck reactions).[1)] Recent findings of remarkable rate acceleration effect by adding silver salts to olefin arylation systems catalyzed by palladium halide complexes implicate involvement of cationic complexes that have higher reactivities than neutral ones in the catalytic processes.[2)] However, only limited studies have been made to compare the reactivities of isolated cationic vis-à-vis neutral organopalladium complexes.[3)] We now report that reactivities of monoorganopalladium complexes toward CO are remarkably enhanced by generating cationic organopalladium complexes $[PdR(s)L_2]^+$ by treating neutral monoorganopalladium complexes *trans*-$PdR(X)L_2$ with $AgBF_4$.



Scheme 1.

Scheme 1 shows an array of neutral monoorganopalladium halide complexes **1a** - **1f** from which cationic organopalladium complexes **2a** - **2f** have been produced by treatment of these complexes with an equivalent of $AgBF_4$ in acetone at -30 °C. Retainment of the trans configuration of the parent neutral $PMe_3$-coordinated complexes in the produced cationic complexes on removal of the halide ligand was confirmed by NMR.$^{4)}$ The cationic methylpalladium complexes, **2a**, **2e**, and **2f**, proved to be stable enough to be isolated as white solid and characterized as acetone-coordinated complexes.$^{5)}$ Other cationic complexes were identified in solutions. Recently, cationic monomethyl- and monoethyl-palladium complexes having chelate ligands have been reported by K. Vrieze,$^{3a)}$ M. Brookhart,$^{6a)}$ and J. L. Spencer,$^{6b)}$ respectively, but so far there are no reports, to our knowledge, of preparation and properties of trans cationic monoalkylpalladium complexes.

All the organopalladium complexes **1** and **2** reacted with atmospheric pressure of CO in acetone-$d_6$ at low temperature to give the corresponding acyl palladium complexes **3** and **4** as characterized by $^1$H- and $^{13}$C-NMR (Scheme 2). Decarbonylation of **3** and **4** were not observed at -30 °C. It was revealed by using $^{13}$CO that the cationic acetyl complex **4** contained the coordinated $^{13}$CO at the site trans to the acetyl group as shown by the $^{13}$C resonance observed at 181 ppm as a triplet.$^{7,\ 8)}$ Both reactions of the neutral complex **1a** and the cationic complex **2a** toward CO followed the pseudo-first order reaction kinetics and the observed rate constant of **2a** ($k_{obsd} = 2.3 \times 10^{-4}\ s^{-1}$) was revealed to be far greater by the factor of $10^2$ than that of **1a** ($k_{obsd} = 2.5 \times 10^{-6}\ s^{-1}$).

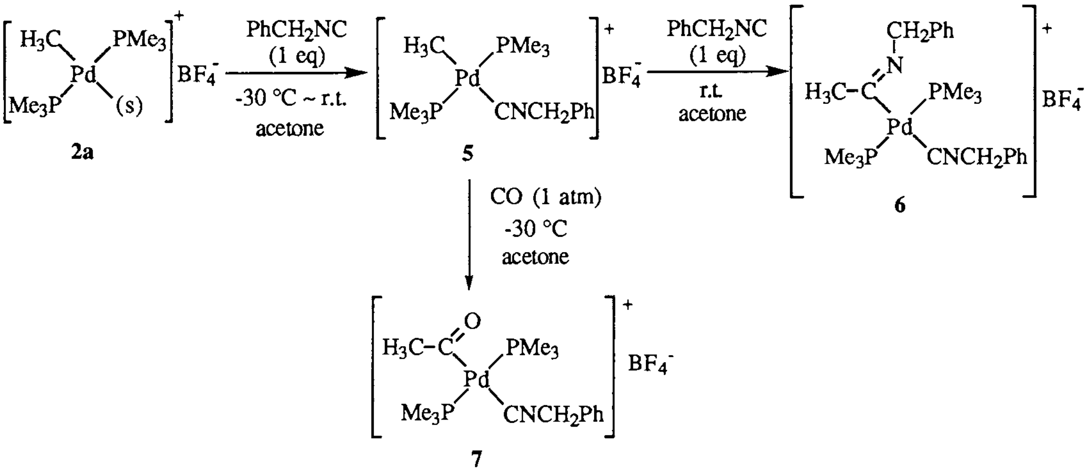


Scheme 2.

We have further compared the reactivity of the cationic *trans*-methylpalladium complex **2a** toward CO with the reactivities of the methylpalladium complexes **2e** and **2f** containing chelating ligands. The methylpalladium complexes **2e** and **2f** having a coordination site available adjacent to the methyl ligand for the incoming CO showed higher reactivities than **2a** having a coordination site trans to the methyl ligand; the half-life period for the reaction of **2a** with CO was about 30 min, whereas those of **2e** and **2f** were less than 10 min under the same conditions.$^{3b)}$

Changing the solvent from acetone-$d_6$ to other strongly coordinating solvents such as acetonitrile-$d_3$ caused the delay in the CO insertion. Addition of 1 eq of trimethylphosphine to **2a** gave $[PdMe(PMe_3)_3]BF_4$ which proved to be unreactive to CO unless the reaction is run at room temperature. The retardation effect on CO insertion by strongly coordinating ligands suggests the requirement of an available coordination site in the cationic complex for CO insertion.[3a)]

The reaction of **2a** with isocyanide that is isoelectronic with CO was also examined. Addition of 1 eq of benzyl isocyanide to **2a** gives an isocyanide-coordinated complex *trans*-$[PdMe(CNCH_2Ph)(PMe_3)_2]^+BF_4^-$ **5** without giving an insertion product even at 25 °C. Complex **5** on further treatment with one more equivalent of benzyl isocyanide gave the isocyaide insertion product **6** whereas the reaction with CO gave the CO insertion product, *trans*-$[Pd(CH_3CO)(CNCH_2Ph)(PMe_3)_2]^+BF_4^-$ **7** (Scheme 3).[7)] These results indicate that isocyanide coordination to the site trans to the methyl group in the trans-methylpalladium complex does not block the further isocyanide or CO insertion into the $CH_3$-Pd bond. We are examining the reaction courses to clarify the isocyanide insertion mechanism from **5**.



Scheme 3.

This study was supported by grant from Nippon Zeon Co. and the Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics No. 05236106 from the Ministry of Education, Science and Culture, Japan.

References

1) R. F. Heck, "*Palladium Reagents in Organic Synthesis*," Academic Press, New York (1985); G. D. Davis, Jr. and A. Hallberg, *Chem. Rev.*, **89**, 1433 (1989).

2) K. Karabelas, C. Westerlund, and A. Hallberg, *J. Org. Chem.*, **50**, 3896 (1985); R. C. Larock and W. H. Gong, *ibid.*, **54**, 2047 (1989); M. M. Abelman and L. E. Overman, *J. Am. Chem. Soc.*, **110**, 2328 (1988); T. Jeffery, *Tetrahedron Lett.*, **33**, 1989 (1992); Y. Sato, S. Watanabe, and M. Shibasaki, *ibid.*, **33**, 2589 (1992); Y. Sato, T. Honda, and M. Shibasaki, *ibid.*, **33**, 2593 (1992).

3) a) G. P. C. M. Dekker, C. J. Elsevier, K. Vrieze, and P. W. N. M. van Leeuwen, *Organometallics*, **11**, 1598 (1992); b) G. P. C. M. Dekker, C. J. Elsevier, K. Vrieze, P. W. N. M. van Leeuwen, and C. F. Roobeek, *J. Organomet. Chem.*, **430**, 357 (1992); c) A. C. Albéniz, P. Espinet, C. Foces-Foces, and F. H. Cano, *Organometallics*, **9**, 1079 (1990); d) F. Kawataka, Y. Kayaki, I. Shimizu, and A. Yamamoto, *Organometallics*, in press.

4) The isolated complexes **2a**, **2e**, and **2f** were not stable enough to be subjected to elemental analysis and were characterized by spectroscopic means. NMR data for **2** are as follows. $^1H$ (270 MHz), $^{31}P\{^1H\}$ (109.4 MHz),

and $^{13}$C{$^{1}$H} NMR (67.9 MHz) were observed in acetone-$d_6$ solutions. **2a**: $^{1}$H NMR δ 0.49 (t, $^{3}J_{PH}$ = 7.1 Hz, 3 H), 1.36 (vt, $J_{PH}$ = 3.3 Hz, 18 H); $^{31}$P{$^{1}$H} NMR δ -13.24 (s); $^{13}$C{$^{1}$H} NMR δ -6.59 (t, $^{2}J_{PC}$ = 5.4 Hz), 12.53 (vt, $J_{PC}$ = 14.8 Hz). **2b**: $^{1}$H NMR δ 1.03 (tt, $^{4}J_{PH}$ = 4.0 Hz, $^{3}J_{HH}$ = 8.0 Hz, 3 H), 1.38 (vt, $J_{PH}$ = 3.3 Hz, 18 H), 1.43-1.63 (m, 2 H); $^{31}$P{$^{1}$H} NMR δ -14.31 (s); $^{13}$C{$^{1}$H} NMR δ 10.20 (br s), 12.58 (vt, $J_{PC}$ = 14.1 Hz), 16.47 (s). **2c**: $^{1}$H NMR δ 1.15 (vt, $J_{PH}$ = 3.5 Hz, 18 H), 6.90-7.13 (m, 3 H), 7.30-7.45 (m, 2 H); $^{31}$P{$^{1}$H} NMR δ -16.34 (s); $^{13}$C{$^{1}$H} NMR δ 12.43 (vt, $J_{PC}$ = 15.2 Hz), 124.73 (s), 129.18 (s), 136.18 (t, $^{3}J_{PC}$ = 5.0 Hz), 146.60 (t, $^{2}J_{PC}$ = 8.1 Hz). **2d**: $^{1}$H NMR δ 1.14 (vt, $J_{PH}$ = 3.7 Hz, 18 H), 2.20 (s, 3 H), 6.91-6.96 (m, 2 H), 7.20-7.25 (m, 2 H); $^{31}$P{$^{1}$H} NMR δ -16.56 (s); $^{13}$C{$^{1}$H} NMR δ 12.45 (vt, $J_{PC}$ = 15.1 Hz), 21.03 (s), 130.03 (s), 133.73 (s), 135.82 (t, $^{3}J_{PC}$ = 4.7 Hz), 141.68 (t, $^{2}J_{PC}$ = 8.7 Hz). **2e**: $^{1}$H NMR δ 0.42 (dd, $^{3}J_{PH}$ = 0.9, 7.2 Hz, 3 H), 2.42-2.64 (m, 2 H), 2.82-3.04 (m, 2 H), 7.55-7.90 (m, 20 H); $^{31}$P{$^{1}$H} NMR δ 39.44 (d, $^{2}J_{PP}$ = 23.4 Hz), 62.89 (d, $^{2}J_{PP}$ = 23.4 Hz). **2f**: $^{1}$H NMR δ 0.20 (dd, $^{3}J_{PH}$ = 1.3, 7.3 Hz, 3 H), 1.53 (d, $^{2}J_{PH}$ = 9.3 Hz, 6 H), 1.71 (d, $^{2}J_{PH}$ = 12.1 Hz, 6 H), 1.80-2.40 (m, 4 H); $^{31}$P{$^{1}$H} NMR δ 25.73 (d, $^{2}J_{PP}$ = 23.5 Hz), 43.52 (d, $^{2}J_{PP}$ = 23.5 Hz).

5) The signal of acetone was observed in the acetonitrile-$d_3$ solution of the isolated complexes in $^{1}$H-NMR; ν(CO) of solvated acetone was observed at 1636 cm$^{-1}$ in the IR spectrum of **2a**.

6) a) M. Brookhart, F. C. Rix, and J. M. DeSimone, *J. Am. Chem. Soc.*, **114**, 5894 (1992); b) F. M. C.-Lewis, L. Mole, A. D. Redhouse, S. A. Litster, and J. L. Spencer, *J. Chem. Soc., Chem. Commun.*, **1991**, 1601.

7) NMR data for **3** - **7** are as follows. $^{1}$H (270 MHz), $^{31}$P{$^{1}$H} (109.4 MHz), and $^{13}$C{$^{1}$H} NMR (67.9 MHz) were observed in acetone-$d_6$ solutions. **3**: $^{1}$H NMR δ 1.35 (vt, $J_{PH}$ = 3.9 Hz, 18 H), 2.31 (t, $^{4}J_{PH}$ = 1.5 Hz, 3 H); $^{31}$P{$^{1}$H} NMR δ -18.02 (s); $^{13}$C{$^{1}$H} NMR δ 14.57 (vt, $J_{PC}$ = 13.7 Hz), 42.70 (t, $^{3}J_{PC}$ = 19.1 Hz), 236.92 (s). **4**: $^{1}$H NMR δ 1.38 (vt, $J$ = 3.3 Hz, 18 H), 2.54 (t, $^{4}J_{PH}$ = 1.5 Hz, 3 H); $^{31}$P{$^{1}$H} NMR δ -18.97 (s); $^{13}$C{$^{1}$H} NMR δ 13.74 (vt, $J_{PC}$ = 14.1 Hz), 39.95 (t, $^{1}J_{PC}$ = 13.0 Hz), 181.38 (t, $^{2}J_{PC}$ = 14.9 Hz), 225.68 (s). **5**: $^{1}$H NMR δ 0.14 (br s, 3 H), 1.50 (s, 18 H), 5.22 (s, 2 H), 7.42-7.60 (m, 5 H); $^{31}$P{$^{1}$H} NMR δ -13.20 (s); $^{13}$C{$^{1}$H} NMR δ -1.71 (s), 14.30 (vt, $J_{PC}$ = 15.3 Hz), 48.92 (t, $^{4}J_{PC}$ = 6.1 Hz), 128.82 (s), 129.33 (s), 130.12 (s), 130.29 (s), 133.32. **6**: $^{1}$H NMR δ 1.47 (br s, 18 H), 2.25 (br s, 3 H), 4.83 (s, 2 H), 5.23 (br s, 2 H), 7.19-7.58 (m, 10 H); $^{13}$C{$^{1}$H} NMR δ 18.61 (vt, $J_{PC}$ = 15.8 Hz), 35.21 (t, $^{3}J_{PC}$ = 9.8 Hz), 51.45 (s), 67.13 (t, $^{4}J_{PC}$ = 6.7 Hz) 130.28 (s), 131.15 (s), 131.34 (s), 132.08 (s), 132.16 (s), 133.05 (s), 136.07 (s), 144.65 (s), 194.78 (s). **7**: $^{1}$H NMR δ 1.44 (br s, 18 H), 2.37 (br s, 3 H), 5.22 (s, 2 H), 7.42-7.60 (m, 5 H); $^{13}$C{$^{1}$H} NMR δ 15.50 (s), 41.99 (br), 49.02 (t, $^{4}J_{PC}$ = 6.5 Hz), 129.43 (s), 129.93 (s), 130.35 (s), 130.49 (s), 133.47 (s), 242.20 (br).

8) I. Tóth and C. J. Elsevier, *J. Am. Chem. Soc.*, **115**, 10388 (1993).

(Received August 29, 1994)