Reactivities of Neutral and Cationic Organopalladium Complexes

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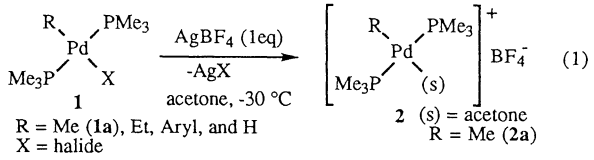
(Received August 30, 1995)

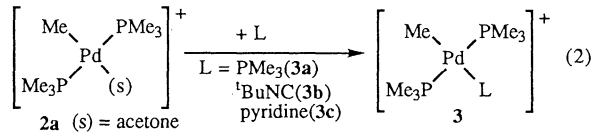
Novel, neutral and cationic monoorganopalladium complexes containing the methyl ligand as well as ethyl ligands having polar substituents have been prepared and their reactivities toward CO insertions have been compared. The results indicate that ready availability of CO coordination site in the complexes is the most important factor in determining the reactivities of the monoorganopalladium complexes toward CO insertion.

In our previous work on the reactivities of alkylpalladium complexes we have observed that the reactivities of the neutral alkylpalladium halide complexes are considerably enhanced by removing the halide ligand with one equivalent of a silver salt to make the alkyl complexes susceptible to β-hydrogen elimination,[1] olefin insertion,[2] and CO insertion[3,4] (eq. 1). A question has remained to be solved whether the enhanced reactivity by removal of the halide ligand is caused by generation of cationic organopalladium complexes having possibly greater propensity toward coordination and subsequent migratory insertion of olefins and CO, or if it is due to the availability of a coordination site created by removal of the halide ligand. The present communication is an attempt to answer the question.



(1)

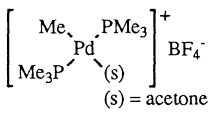
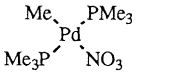
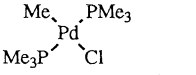
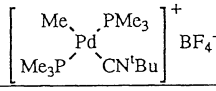
Neutral methylpalladium complexes having halide ligand **1**, and cationic solvent-coordinated complexes **2** ((s) = methanol, acetone, and acetonitrile) were prepared and the reactivities of **2** were compared with those of the cationic methylpalladium complexes coordinated with stronger donors **3a** - **3c**.



(2)

Comparison of the relative CO insertion rate into the C-Pd bond in complexes **1**-**4** (Table 1) shows that the electric charge is not the dominant factor in determining the reactivity of the methylpalladium complex toward CO insertion. The cationic, isocyanide-coordinated complex **3b** proved to be less reactive to CO insertion than the neutral chloride complex **1** by a factor of 10. The CO insertion rate constant k_{obsd} of the solvent-coordinated methylpalladium complexes at -20 °C increased in the order of acetonitrile-d_3 (1.4×10^{-4} s^{-1}) < acetone-d_6 (2.3×10^{-4} s^{-1}) < dichloromethane-d_2 (1.3×10^{-3} s^{-1}) indicating that the strongly coordinating solvent tends to retard the CO insertion. In the migratory CO insertion into the methyl-palladium bond, availability of the site cis to the methyl group is essential for the reaction to proceed.[5] Thus replacement of the strongly coordinating ligand PMe_3 with more dissociating $PMePh_2$ ligand at the site cis to the methyl group caused increase in the CO insertion rate constant at -20 °C from 2.3×10^{-4} to 5.8×10^{-4} s^{-1} in acetone-d_6.

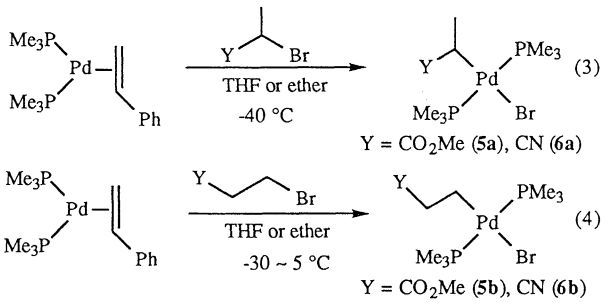
Table 1. Rate constants for CO insertion (-20 °C)

Complex		k_{obsd}/s^{-1}
 (s) = acetone	**2a**	2.3×10^{-4}
	**4**	5.9×10^{-5}
	**1**	2.5×10^{-6}
	**3b**	2.3×10^{-7}

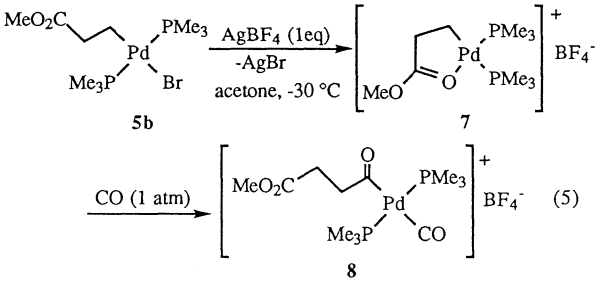
Furthermore, addition of 3.4 eq of $AgBF_4$ to **2a** caused the enhancement in reactivity for the CO insertion from k_{obsd} = 2.3×10^{-4} to 9.8×10^{-4} s^{-1} at -20 °C. The treatment of **1a** with an excess of $AgBF_4$ gave a silver-phosphine complex with the composition of $Ag(PMe_3)BF_4$ and a solvent-coordinated methyl-mono(phosphine)palladium complex. The methyl-mono-(phosphine)palladium complex reverted to **2a** by addition of 1 eq of PMe_3. Cationic tris(trimethylphosphine) complex **3a** also reacts with 1 eq of $AgBF_4$ to give **2a** and the above-mentioned silver-phosphine complex.

The nature of the counter anion associated with the cationic complex also affects the CO insertion. Thus usage of OTf having a higher coordination ability,[6] instead of BF_4 or PF_6, caused decrease in the reactivity toward CO insertion from k_{obsd} = 2.3×10^{-4} to 1.1×10^{-4} s^{-1}. A new methylpalladium complex having the NO_3 ligand, *trans*-$[PdMe(NO_3)(PMe_3)_2]$**4**,[7] was obtained by treatment of **1a** with $AgNO_3$ in the presence of water. The NO_3 ligand coordinated to palladium center dissociates in H_2O solution as indicated by conductometry. Addition of water to the acetone solution (1:1) causes the rate enhancement for the CO insertion.by a factor of 2.3 implying the increased reactivity of the water-coordinated cationic complex than the neutral NO_3-bound complex.

In our attempt to expand the scope of the chemistry of monoorganopalladium complexes we have prepared monoalkylpalladium complexes substituted with a polar functional group,[8] **5a** and **5b**, by treating a styrene-coordinated Pd(0) complex with methyl α- and β-bromopropionates.[9,10] (eq. 3, 4) Treatment of the Pd(0) complex with α- and β-bromopropionitrile similarly yielded ethylpalladium complexes substituted with the CN group at the α- and the β- positions, **6a** and **6b**.[11,12]



In complexes **5** and **6** having the β-hydrogens the decomposition route through the β-hydrogen elimination is blocked by two PMe_3 ligands flanking the alkyl group. Removal of the bromide ligand at the position trans to the alkyl group did not lead to the β-hydrogen elimination but gave the stable, cationic carbonyl-coordinated five-membered complex **7**.[13] The treatment of **7** with CO (1 atm) at -30 °C gave the cationic CO-bound acylpalladium complex **8** (eq. 5).[14] The bond between the acyl carbonyl group and the cationic palladium center in **7** seems to be weak as judged by ready insertion of CO at atmospheric pressure. The ready conversion of complex **7** to the CO-coordinated *trans*-acylpalladium complex **8** implies the mobility of the PMe_3 ligand in the square planar configurations.



In conclusion, for enhancing the reactivity of a monoalkylpalladium complex availability of a coordination site for the incoming CO cis to the alkyl group to be inserted is crucial. As shown in the present and previous studies the employment of the less dissociating PMe_3 ligand made the model study simpler and provided information otherwise unavailable. However, in the real catalytic system where the more dissociating ligands are used, we have to take into account the dissociation of the phosphine ligand providing a free coordination site.

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 and Notes

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7 **4**: ^1H NMR (270 MHz, acetone-d_6) δ 1.31 (18H, vt, J_{PH} = 3.3 Hz), 0.22 (3H, t, J_{PH} = 7.0 Hz); $^{31}P\{^1H\}$ NMR (109.4 MHz, acetone-d_6) δ -12.15 (s); $^{13}C\{^1H\}$ NMR (67.9 MHz,acetone-d_6) δ 12.65 (vt, J_{PC} = 14.2 Hz), -10.96 (t, J_{PC} = 6.1 Hz); Anal. Found: C, 25.29; H, 6.40; N, 3.99%. Calcd for $C_7H_{21}NO_3P_2Pd$: C, 25.07; H, 6.32; N, 4.18%.

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9 A. Yamamoto, *J. Organomet. Chem.*, **500**, 337 (1995).

10 **5a**: ^1H NMR (270 MHz, acetone-d_6) δ 3.51 (3H, s), 2.97 (1H, tq, J_{HH} = 7.3 Hz, J_{PH} = 7.1 Hz), 1.51 (18H, vt, J_{PH} = 3.3 Hz), 1.18 (3H, dt, J_{HH} = 7.3 Hz, J_{PH} = 3.3 Hz); $^{31}P\{^1H\}$ NMR (109.4 MHz, acetone-d_6) δ -14.37 (s); $^{13}C\{^1H\}$ NMR (67.9 MHz, acetone-d_6) δ 180.84, 51.16, 20.92, 18.07 (t, J_{PC} = 2.7 Hz), 15.22 (vt, J_{PC} = 15.0 Hz); IR (KBr) 1682 cm^{-1} ($\nu_{C=O}$); Anal. Found: C, 28.45; H, 5.87%. Calcd for $C_{10}H_{25}BrO_2P_2Pd$: C, 28.30; H, 5.94%. **5b**: ^1H NMR (270 MHz, acetone-d_6) δ 3.57 (3H, s), 2.34 (2H, tt, J_{HH} = 7.9 Hz, J_{PH} = 7.9 Hz), 1.50 (2H, m), 1.47 (18H, vt, J_{PH} = 3.3 Hz); $^{31}P\{^1H\}$ NMR (109.4 MHz, acetone-d_6) δ -14.22 (s); $^{13}C\{^1H\}$ NMR (67.9 MHz, acetone-d_6) δ 174.81, 51.94, 36.89, 14.06 (vt, J_{PC} = 14.5 Hz), 10.63 (t, J_{PC} = 2.7 Hz); IR (KBr) 1727 cm^{-1} ($\nu_{C=O}$); Anal. Found: C, 28.48; H, 5.87%. Calcd for $C_{10}H_{25}BrO_2P_2Pd$: C, 28.30; H, 5.94%.

11 **6a**: ^1H NMR (270 MHz, acetone-d_6) δ 2.38 (1H, tq, J_{HH} = 7.3 Hz, J_{PH} = 7.7 Hz), 1.57 (18H, vt, J_{PH} = 3.5 Hz), 1.30 (3H, dt, J_{HH} = 7.3 Hz, J_{PH} = 3.0 Hz); $^{31}P\{^1H\}$ NMR (109.4 MHz, acetone-d_6) δ -12.96 (s); $^{13}C\{^1H\}$ NMR (67.9 MHz, acetone-d_6) δ 130.17, 18.72, 14.55 (vt, J_{PC} = 15.1 Hz), -1.83 (t, J_{PC} = 2.4 Hz); IR (KBr) 2189 cm^{-1} ($\nu_{C\equiv N}$); Anal. Found: C, 27.86; H, 5.48; N, 3.64%. Calcd for $C_9H_{22}BrNP_2Pd$: C, 27.63; H, 5.67; N, 3.58%. **6b**: ^1H NMR (270 MHz, acetone-d_6) δ 2.55 (2H, t, J_{HH} = 7.7 Hz), 1.52 (18H, vt, J_{PH} = 3.3 Hz), 1.43 (2H, m); $^{31}P\{^1H\}$ NMR (109.4 MHz, acetone-d_6) δ -13.68 (s); $^{13}C\{^1H\}$ NMR (67.9 MHz, acetone-d_6) δ 122.65, 19.52, 14.19 (vt, J_{PC} = 14.8 Hz), 8.87 (t, J_{PC} = 3.4 Hz); IR (KBr) 2233 cm^{-1} ($\nu_{C\equiv N}$); Anal. Found: C, 27.66; H, 5.66; N, 3.58%. Calcd for $C_9H_{22}BrNP_2Pd$: C, 27.63; H, 5.67; N, 3.58%.

12 The reaction of $PdH(Cl)(PMe_3)_2$ and methyl acrylate or acrylonitrile also afforded the ethyl palladium complexes having the polar substituent at the α position; but the yield was very low.

13 **7**: ^1H NMR (270 MHz, acetone-d_6) δ 3.84 (3H, s), 3.01 (2H, dt, J_{HH} = 7.3 Hz, J_{PH} = 7.5 Hz), 1.54 (9H, d, J_{PH} = 11.4 Hz), 1.50 (2H, m), 1.40 (9H, d, J_{PH} = 8.4 Hz); $^{31}P\{^1H\}$ NMR (109.4 MHz, acetone-d_6) δ 0.30 (d, J_{PP} = 40 Hz), -21.10 (d, J_{PP} = 40 Hz); $^{13}C\{^1H\}$ NMR (67.9 MHz, acetone-d_6) δ 192.27(d, J_{PC} = 13.4 Hz), 54.90, 37.93 (d, J_{PC} = 5.3 Hz), 21.20 (d, J_{PC} = 90.0 Hz), 16.57 (dd, J_{PC} = 37.7, 4.0 Hz), 14.70 (d, J_{PC} = 21.5 Hz); IR (KBr) 1625 cm^{-1} ($\nu_{C=O}$); Anal. Found: C, 27.87; H, 5.78%. Calcd for $C_{10}H_{25}BF_4O_2P_2Pd$: C, 27.78; H, 5.83%.

14 **8**: ^1H NMR (270 MHz, acetone-d_6) δ 3.60 (3H, s), 3.20 (2H, t, J_{HH} = 5.9 Hz), 2.45 (2H, t, J_{HH} = 5.9 Hz), 1.48 (18H, vt, J_{PH} = 3.9 Hz); $^{31}P\{^1H\}$ NMR (109.4 MHz, acetone-d_6) δ -18.80 (s); $^{13}C\{^1H\}$ NMR (67.9 MHz, acetone-d_6) δ 229.46, 180.76 (t, J_{PC} = 17.5 Hz), 173.94, 52.30, 49.84, 14.27 (vt, J_{PC} = 4.5 Hz).