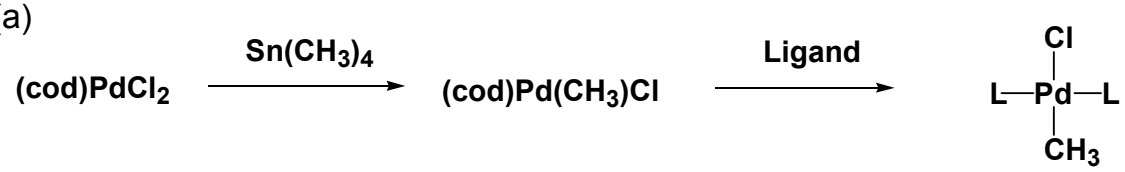
Supplementary Material for Chemical Communications

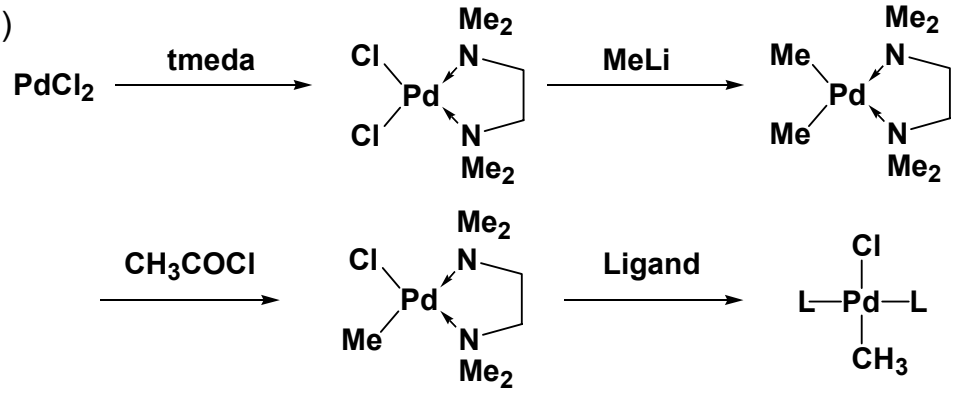
Supporting Information 1 M. Tada et al.

Synthesis steps for the Pd precursors

(a)



(b)



$PdMeCl(P(O\text{-}iPr)_3)_2$

0.2 g of (cod)PdMeCl was dissolved in 5 ml of absolute CH_2Cl_2 and cooled to 263 K under nitrogen atmosphere. 0.31 g of $P(O\text{-}iPr)_3$ was added to the solution and the reaction mixture was stirred at 273 K for 2 h. The solvent was evaporated under vacuum. Obtained crude crystal was recrystalized with n-hexane.

^{1}H NMR ($CDCl_3$): δ=5.06 (6H, $P(O\text{-}CH(CH_3)_2)_3$, m), 1.27 (36H, $P(O\text{-}CH(CH_3)_2)_3$, d), 0.74 (3H, $Pd\text{-}CH_3$, s). ^{13}C NMR: 71.27 (O*C*H-), 24.69 (-OCH-(*C*H_3)$_2$), 0.96 (Pd-*C*H_3), ^{31}P: 115.66.

PdClMe(tmeda)

$PdMe_2$(tmeda) 0.53 g was dissolved in benzene 30 ml under nitrogen atmosphere and cooled at 273 K. Acetyl chrolide 0.2 ml was added to the solution and stirred at 273 K for 1 h. The solvent was evaporated, and obtained solid was washed with n-pentane three times. Recrystalization was performed with CH_2Cl_2.

^{1}H NMR ($CDCl_3$): δ=2.49-2.78 (4H, -C*H*$_2$-, m), 2.66 (6H, N(C*H*$_3$)$_2$, s), 2.57 (6H, N(C*H*$_3$)$_2$, s), 0.49 (3H, Pd-C*H*$_3$, s). Anal. Calcd for PdClMe(tmeda): C, 30.79; H, 7.01; N, 10.26. Found: C, 30.57; H, 6.90; N, 10.17.

PdClMe(PMe_2Ph)$_2$

PdMeCl(tmeda) 0.35 g was dissolved in absolute CH_2Cl_2 10 ml under nitrogen atmosphere, and PMe_2Ph 0.38 ml was added to the solution. The reaction mixture was stirred for 1 h, and the solvent was evaporated under vacuum. Recrystalization was carried out with acetone.

^{1}H NMR ($CDCl_3$): δ=7.36-7.65 (10H, Ph, m), 1.72 (12H, PMe_2, d), 0.01 (3H, Pd-Me, s). ^{31}P NMR: -1.44. Anal. Calcd for PdClMe(PMe_2Ph)$_2$: C, 47.13; H, 5.82; N, 0. Found: C, 47.09; H, 5.77; N, 0.

(dppf)PdClMe

(cod)PdMeCl 0.20 g was dissolved in 5 ml of toluene under N_2 atmosphere, to which dppf (1,1-bis(diphenylphosphino)ferrocene) 0.42 g was added, followed by stirring for 1 h. The solvent was evaporated under vacuum, and obtained crude crystal was recrystalized with CH_2Cl_2.

^{1}H NMR ($CDCl_3$): 7.22-7.60 (20H, Ph, m), 4.46 (2H, Cp, s), 4.41 (2H, Cp, s), 4.21 (2H, Cp, s), 3.75 (2H, Cp, s), 0.75 (3H, Pd-Me, s).

(cyclohexylamine)$_2$PdClMe

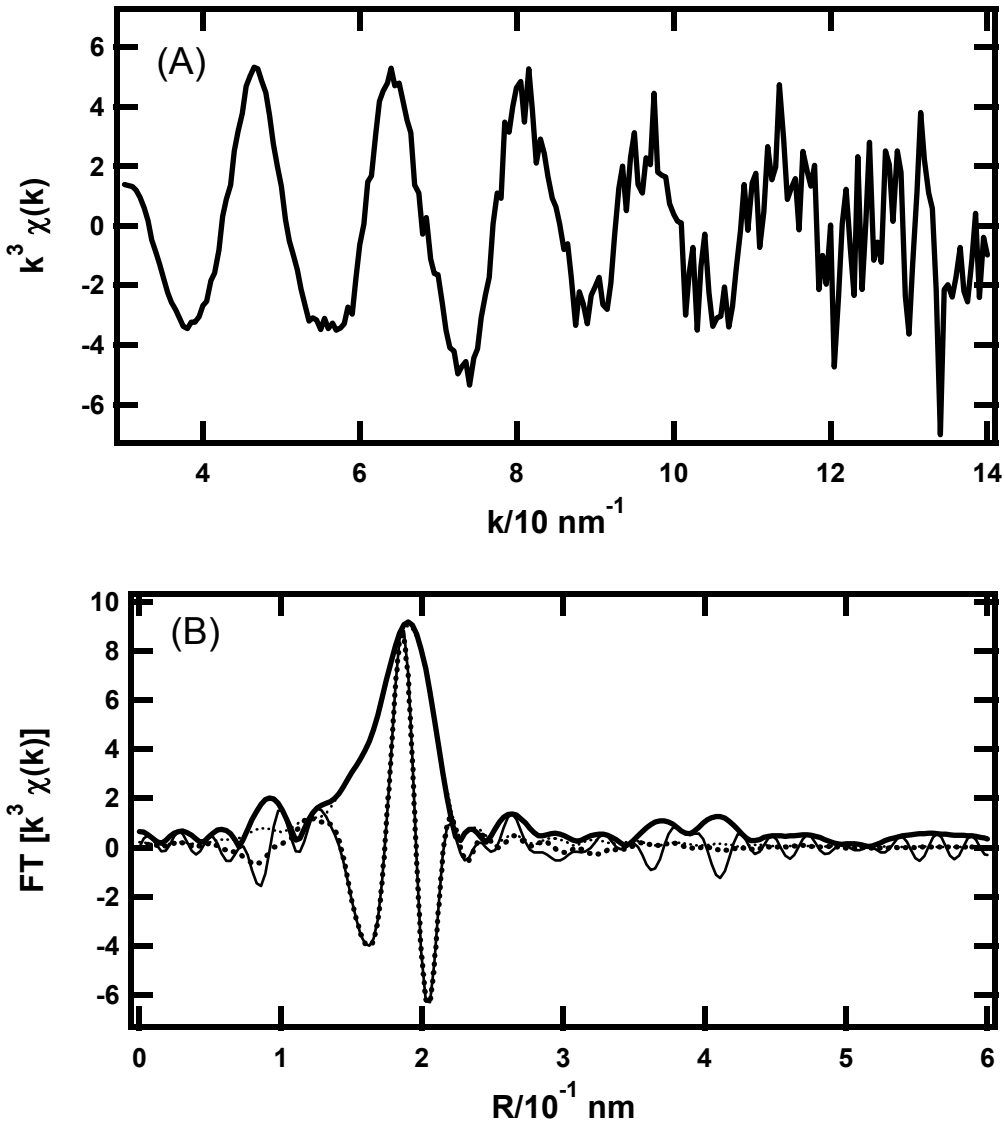
(cod)PdMeCl 0.20 g was dissolved in 5 ml of CH_2Cl_2 under nitrogen atmosphere, and cyclohexylamine 0.15 g was added to the solution. White precipitate was formed immediately, and the solvent was evaporated under vacuum. Recrystalization was performed with acetone.

^{1}H NMR ($CDCl_3$): 2.77 (2H, NH_2-C*H*-, m), 2.24 (4H, p-CH_2-, m), 1.32 (8H, o-CH_2-, m), 1.11 (8H, m-CH_2-, m), 0.32 (3H, Pd-CH_3, s).

(2-methylpiperidine)$_2$PdClMe

(cod)PdMeCl 0.20 g was dissolved in 5 ml of CH_2Cl_2 under nitrogen atmosphere. 2-methylpiperidine 0.15 g was added to the solution, and stirred for 1 h. The solvent was evaporated under vacuum. Recrystalization was carried out with acetone.

^{1}H NMR ($CDCl_3$): 2.95, 3.38 (4H, o-CH_2-, m), 2.75 (2H, NH-C*H*-, m), 1.01, 1.71 (4H, NH-CH-CH_2-, m), 1.20-1.35 (4H, p-CH_2-, m), 1.45 (6H, NH-CHCH_3-, d), 1.49-1.58 (4H, m-CH_2-, m), 0.26 (3H, Pd-CH_3, s). ^{13}C NMR: 54.81 (NH-*C*H_2-), 51.44 (NH-*C*HCH$_3$), 34.66 (NH-CHCH$_3$-*C*H$_2$-), 26.73 (NH-CH$_2$-*C*H$_2$-), 24.4 (NH-CH$_2$-CH$_2$-*C*H$_2$-), 23.42 (NH-CH*C*H$_3$-), -3.04 (Pd-*C*H$_3$). Anal. Calcd for (2-methylpiperidine)$_2$PdClMe: C, 43.95; H, 8.23; N, 7.89. Found: C, 43.41; H, 8.47; N, 7.82.



Supporting Information Pd K-edge EXAFS oscillation (A) and its Fourier transformed spectrum (B) of supported Pd-P (P: PMe_2Ph) complex measured at 15 K. ——: Absolute; ——: imaginary; ▪▪▪▪▪ and ·····: fitting for the absolute and imaginary parts, respectively.

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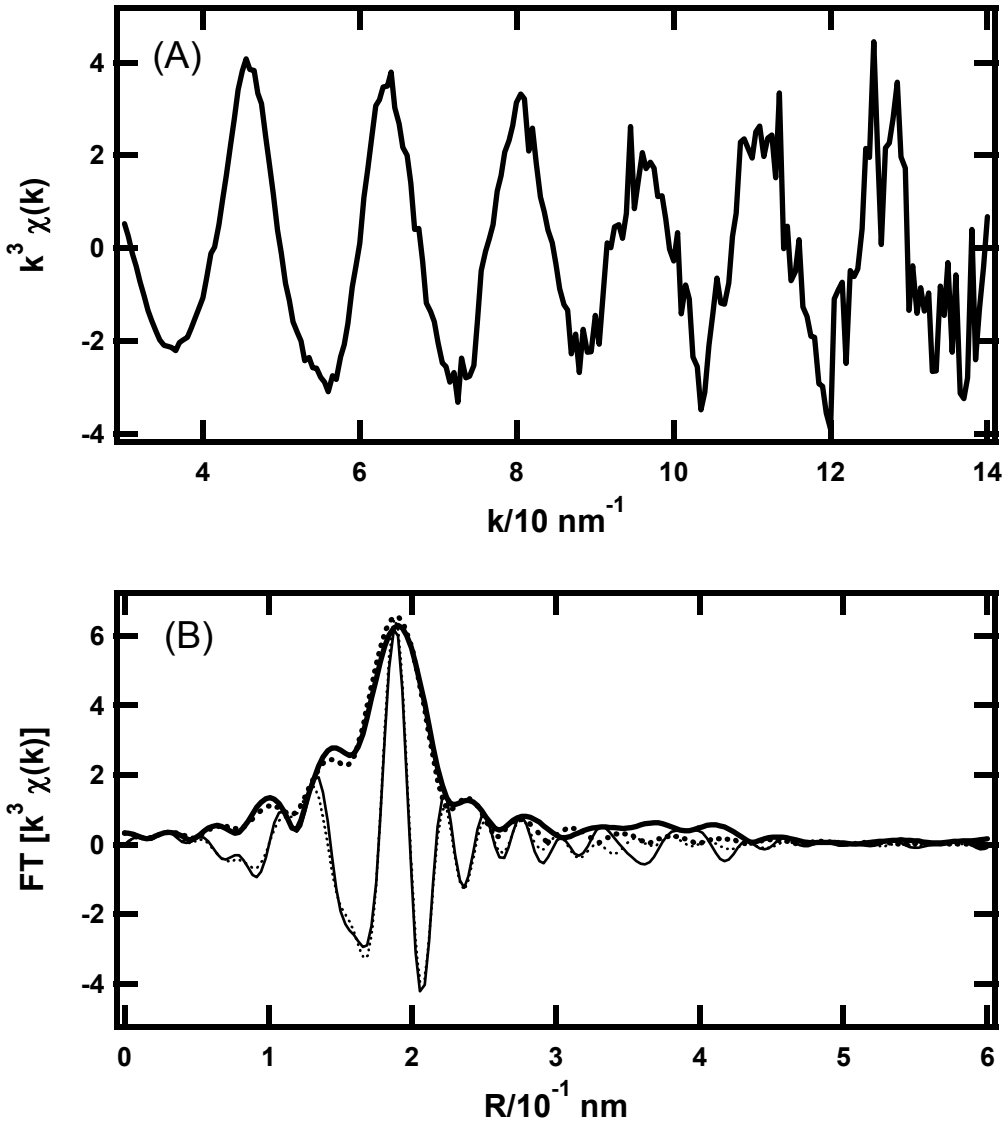

Supporting Information Pd K-edge EXAFS oscillation (A) and its Fourier transformed spectrum (B) of supported Pd-N (N: methylpiperidine) complex measured at 15 K. ——: Absolute; ——: imaginary; ▪▪▪▪▪ and ·····: fitting for the absolute and imaginary parts, respectively.

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