Supplementary Material (ESI) for Dalton Transactions

Electronic supplementary information

N-Heterocyclic carbene ligands bearing hydrophilic and/or hydrophobic chains: Rh(I) and Pd(II) complexes and their catalytic activity

Hidetoshi Ohta,[a,b] Tetsuaki Fujihara[a] and Yasushi Tsuji*[a]

[a] Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8510, Japan. [b] Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

* To whom correspondence should be addressed.

Fax: +81-75-383-2514; Tel: +81-75-383-2515; E-mail: ytsuji@scl.kyoto-u.ac.jp

^{1}H NMR Spectral Data of [PdCl(η^3-C_3H_5)(1a-d)].

[PdCl(η^3-C_3H_5)(**1a**)]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (s, 2H, NHC), 6.59 (s, 4H, Ar), 5.31-5.16 (m, 5H, CH_2-NHC + C_3H_5), 4.24 (d, J = 7.3 Hz, 1H, C_3H_5), 4.14-4.09 (m, 12H, OCH_2), 3.82-3.75 (m, 12H, OCH_2), 3.71-3.62 (m, 60H, OCH_2), 3.54-3.52 (m, 12H, OCH_2), 3.36-3.35 (m, 18H, OCH_3), 3.20-3.15 (m, 2H, C_3H_5), 2.12 (d, J = 12.2 Hz, 1H, C_3H_5).

[PdCl(η^3-C_3H_5)(**1b**)]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.87 (d, J = 2.0 Hz, 1H, NHC), 6.84 (d, J = 2.0 Hz, 1H, NHC), 6.60 (s, 2H, Ar), 6.53 (s, 2H, Ar), 5.33-5.15 (m, 5H, CH_2-NHC + C_3H_5), 4.25 (d, J = 7.8 Hz, 1H, C_3H_5), 4.14-4.09 (m, 6H, OCH_2), 3.95-3.89 (m, 6H, OCH_2), 3.82-3.75 (m, 6H, OCH_2), 3.70-3.61 (m, 30H, OCH_2), 3.54-3.51 (m, 6H, OCH_2), 3.36-3.35 (m, 9H, OCH_3), 3.20-3.17 (m, 2H, C_3H_5), 2.10 (d, J = 12.2 Hz, 1H, C_3H_5), 1.79-1.68 (m, 6H, CH_2), 1.45-1.41 (m, 6H, CH_2), 1.35-1.22 (m, 48H, CH_2), 0.87 (t, J = 6.8 Hz, 9H, CH_3).

[PdCl(η^3-C_3H_5)(**1c**)]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (s, 2H, NHC), 6.52 (s, 4H, Ar), 5.33-5.16 (m, 5H, CH_2-NHC + C_3H_5), 4.25 (d, J = 7.3 Hz, 1H, C_3H_5), 3.94-3.89 (m, 12H, OCH_2), 3.20-3.15 (m, 2H, C_3H_5), 2.07 (d, J = 12.2 Hz, 1H, C_3H_5), 1.79-1.68 (m, 12H, CH_2), 1.45-1.41 (m, 12H, CH_2), 1.33-1.22 (m, 96H, CH_2), 0.87 (t, J = 6.8 Hz, 18H, CH_3).

[PdCl(η^3-C_3H_5)(**1d**)]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.89 (s, 2H, NHC), 6.60 (s, 4H, Ar), 5.36-5.26 (m, 5H,

CH_2-NHC + C_3H_5), 4.27 (d, J = 7.7 Hz, 1H, C_3H_5), 3.83 (s, 12H, OCH_3), 3.80 (s, 6H, OCH_3), 3.27-3.12 (m, 2H, C_3H_5), 2.15 (d, J = 11.8 Hz, 1H, C_3H_5).

Calculation.

Optimized structures of **5a** and [PdCl(η^3-C_3H_5)(**1a**)] were obtained by ONIOM calculations.[1] In the ONIOM calculation, the molecular system of **5a** or [PdCl(η^3-C_3H_5)(**1a**)] was divided into two layers. The high layers were assigned to **5a** with a RhCl(COD)($C_3H_2N_2$) core and [PdCl(η^3-C_3H_5)(**1a**)] with a PdCl(η^3-C_3H_5)($C_3H_2N_2$) core for B3LYP[2]/LANL2DZ[3] calculation. The low layers contain the rest parts of **5a** and [PdCl(η^3-C_3H_5)(**1a**)] for molecular mechanics calculation using UFF force field.[4] All calculations were performed with the Gaussian 03 program[5] on a HIT HPC-IA642/SS 1.3/3D-4G.

Optimized Structure of [PdCl(η^3-C_3H_5)(1a)] Calculated by ONIOM Method.

At first, the molecular structure of [PdCl(η^3-C_3H_5)(**1a**)] was optimized with the TEG chains keeping anti conformations. The resulting optimized structure (local minimum) is shown in Figure S1(a). During the conformation analysis of [PdCl(η^3-C_3H_5)(**1a**)], it was found that the significantly folded structure shown in Figure S1(b) is much more stable and close to global minimum: calculated energy difference between the structure in Figure S1(a) and S1(b) is 17.2 kcal mol^{-1}.

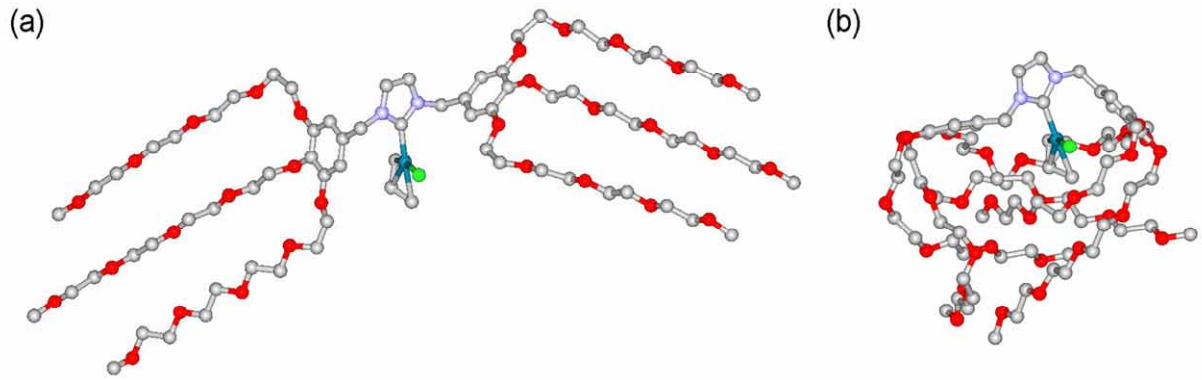

Figure S1. Optimized structures of [PdCl(η^3-C_3H_5)(**1a**)] [(a) extended and (b) folded structures] calculated by ONIOM (B3LYP/LANL2DZ:UFF).

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