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Synthesis, Structures, and Catalytic Properties of Ionic Metallacyclodimeric Palladium(II) Complexes

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Metallacyclodimeric complexes of $[(Me_4en)Pd(L)]_2(ClO_4)_4$ (Me_4en = *N,N,N′,N′*-tetramethylethylenediamine; L = dimethylbis(4-pyridyl)silane (dmps), methylvinylbis(4-pyridyl)silane (mvps)) have been synthesized, and their structures have been characterized by X-ray single crystallography. The skeletal structures consist of one 20-membered metallamacrocycle, two 5-membered metallacycles, and four pyridyl groups. The local geometry around the palladium(II) ion approximates to a typical square planar arrangement with four nitrogen donors. Delicate difference in catalytic effects on hydrogenation was investigated based on the structure of catalyst and substrates.

Key Words : Dimethylbis(4-pyridyl)silane, Hydrogenation catalysis, Metallacyclodimer, Methylvinylbis(4-pyridyl)silane, Palladium(II) complexes

Introduction

Various metallamacrocyclic compounds have been synthesized and characterized for functional supramolecular materials that can be utilized for molecular machines, switches, recognition, selective transformation, drug delivery systems, biomimetics, storage, and catalysts.[1-10] Such metallamacrocycles have been designed based on the coordination geometry of metal ions, the binding sites of donating atoms, the reactivity, the charge, and the length of the spacers. Notably, some palladium(II) complexes of silicon-containing pyridyl ligands have contributed to susceptible coordination materials such as catalysts, rectangular building blocks, submicrospheres, desirable morphology, and "magic ring" with the associative/dissociative dual character of Pd-N bond.[11-15] The silicon-containing pyridyl spacer ligands have been found to be useful for the synthesis of target skeletons since they are adjustable in bridging ability and length, possess flexible angles around silicon, and are conformationally nonrigid.[16-20] Certainly, some palladium(II) complexes have been known to be very good catalysts for various organic reactions.[21] Nonetheless, the catalytic reaction of well-defined metallamacrocycles remains an important issue with regard to the development of advanced materials.[22,23] In order to expand the systematic tendency of metallacyclodimers according to the organic chains attached to silicon as well as the external conditions, we report the construction, structure, and catalytic effects of ionic metallamacrocyclodimeric palladium(II) complexes. The palladium(II) ion as an angular directional unit has been found to be useful for the synthesis of desirable metallacyclic skeletons.[15] In this context, one crucial aim of the present study was to explore the catalytic behavior of the metallamacrocyclic palladium(II) complexes.

Experimental Section

Materials and Measurements. Potassium tetrachloropalladate(II), *N,N,N′,N′*-tetramethylethylenediamine (Me_4en), and various dialkyldichlorosilanes were purchased from Aldrich, and used without further purification. Dimethylbis(4-pyridyl)silane (dmps) was prepared according to the literature method.[20] $(Me_4en)PdCl_2$ was prepared according to the procedure described in the literature.[24] ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Varian Mercury Plus 300, the chemical shifts were relative to the internal $SiMe_4$. Infrared spectra were obtained on a Nicolet 380 FT-IR spectrophotometer with samples prepared as KBr pellets. Elemental microanalyses (C, H, N) were performed on solid samples in the Advanced Analytical Division at KBSI, using a Vario-EL analyzer.

Methylvinylbis(4-pyridyl)silane (mvps). *n*-Butyllithium (14 mL, 35 mmol, 2.5 M solution in hexane) was added to a solution of 4-bromopyridine (5.21 g, 33 mmol) in dry diethyl ether (60 mL) under nitrogen gas at −78 °C, at which temperature the resulting mixture was stirred for 1.5 h. At 0 °C, dichloromethylvinylsilane (2.11 mL, 16 mmol) was slowly added to the yellow suspension, and stirred for 10 h. Distilled water (50 mL) was added into the reaction solution, and the organic solution layer was separated. The organic solution was washed with water several times, and then was dried over $MgSO_4$. The crude product was purified by column chromatography on silica gel with ethyl acetate. The solvent was evaporated to obtain a viscous liquid in 63% yield (2.36 g). Anal. Calc. for $C_{13}H_{14}N_2Si$: C, 68.98; H, 6.23; N, 12.38%. Found: C, 68.90; H, 6.31; N, 12.21%. ^1H NMR ($CDCl_3$, 300 MHz) δ 0.70 (3H, s), 5.88 (1H, dd, J = 3.3 Hz, 20.4 Hz), 6.29 (1H, dd, J = 3.6 Hz, 14.7 Hz), 6.55 (1H, dd, J = 14.4 Hz, 20.4 Hz), 7.47 (4H, d, J = 6.1 Hz), 8.86 (4H, d, J = 6.1

Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) δ −5.21, 129.29, 132.42, 137.43, 144.61, 149.11. IR (KBr, cm^{-1}): 504 (m), 636 (m), 734 (m), 787 (s), 1124 (s), 1402 (s), 1583 (s), 2960 (m), 3053 (m).

[(Me$_4$en)Pd(dmps)]$_2$(ClO$_4$)$_4$·2(Me$_2$CO). (Me_4en)$PdCl_2$ (29.4 mg, 0.01 mmol) was suspended in distilled water (10 mL). $AgClO_4$ (41.5 mg, 0.02 mmol) was added in to the suspension, and the reaction mixture was stirred for 2 h at 40 °C. After removal of AgCl by filtration, dmps (21.4 mg, 0.01 mmol) in acetone (10 mL) was slowly added into the filtrate. The mixture was refluxed for 2 h and cooled. Then the reaction mixture was slowly evaporated for 2 days to obtain pale yellow crystals of [(Me_4en)Pd(dmps)]$_2$(ClO_4)$_4$·2(Me_2CO) in 80% yield. Anal. Calc. for $C_{42}H_{72}Cl_4N_8O_{18}Pd_2Si_2$: C, 36.35; H, 5.23; N, 8.07%. Found: C, 36.10; H, 5.20; N, 8.01%. ^{1}H NMR (Me_2CO-d_6, 300 MHz) δ 0.80 (12H, s), 2.78 (24H, s), 3.23 (8H, s), 7.89 (8H, d, J = 3 Hz) 9.16 (8H, d, J = 3 Hz). IR (KBr, cm^{-1}): 1089 (s, ν(ClO_4)).

[(Me$_4$en)Pd(mvps)]$_2$(ClO$_4$)$_4$·2(Me$_2$CO). Pale yellow crystals of [(Me_4en)Pd(mvps)]$_2$(ClO_4)$_4$·2(Me_2CO) was obtained in the same manner as [(Me_4en)Pd(dmps)]$_2$(ClO_4)$_4$·2(Me_2CO) in 86% yield. Anal. Cald. for $C_{44}H_{72}Cl_4N_8O_{18}Pd_2Si_2$: C, 37.43; H, 5.14; N, 7.94%. Found: C, 37.10; H, 5.09; N, 7.89%. ^{1}H NMR (CD_3CN, 300 MHz) δ 0.80 (6H, s), 2.52 (24H, s), 2.94 (8H, s), 6.06-6.16 (2H, m), 6.43-6.51 (2H, m), 6.57-6.72 (2H, m), 7.66 (8H, d, J = 6 Hz), 8.77 (8H, d, J = 6 Hz). IR (KBr, cm^{-1}): 1089 (s, ν(ClO_4)).

Crystallographic Structure Determinations. X-ray data were collected on a Bruker SMART automatic diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and a CCD detector at 173 K. Thirty six frames of two dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. The absorption effects were corrected using the multi-scan method. The structures were solved using the direct method (SHELXS 97) and refined by full-matrix least squares techniques (SHELXL 97).[25] The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. The crystal parameters and procedural information corresponding to the data collection and structure refinement are listed in Table 1. Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (CCDC-867731 and 867732 for [(Me_4en)Pd(dmps)]$_2$(ClO_4)$_4$ and [(Me_4en)Pd(mvps)]$_2$(ClO_4)$_4$, respectively). The data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/perl/catreq/catreq.cgi (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk).

Hydrogenation Reaction. To a solution of cyclohexene (1 mL) or 1-hexene (1 mL) in *N,N*-dimethylformamide (10 mL), [(Me_4en)Pd(dmps)]$_2$(ClO_4)$_4$·2(Me_2CO) (31.8 mg, 0.25 mol %) or [(Me_4en)Pd(mvps)]$_2$(ClO_4)$_4$·2(Me_2CO) (32.4 mg, 0.25 mol %) was added. Subsequently, hydrogen gas (40 psi) was bubbled into the solution for 3 h at room temperature. After then, diethyl ether (20 mL) was added into the solution to yield pale yellow catalysts as a solid. The filtrate was extracted with water several times, dried over $MgSO_4$, and evaporated by rotary evaporator, and the conversion yield of the products was determined by ^{1}H NMR in $CDCl_3$.

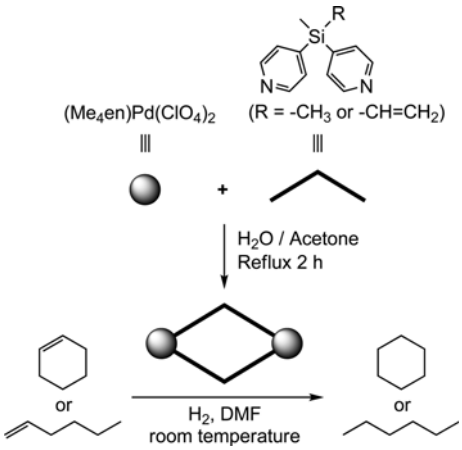
Results and Discussion

Synthesis and Characterization. As shown in Scheme 1, the ionic metallacyclodimeric palladium(II) complexes, [(Me_4en)Pd(L)]$_2$(ClO_4)$_4$ (L = dimethylbis(4-pyridyl)silane (dmps); methylvinylbis(4-pyridyl)silane (mvps)), were prepared by the reaction of (Me_4en)Pd(ClO_4)$_2$ with L, followed by slow evaporation of solvent, yielding pale yellow single crystals suitable for X-ray crystallographic analysis. IR, ^{1}H

Table 1. Crystal data for [(Me_4en)Pd(dmps)]$_2$(ClO_4)$_4$·2(Me_2CO) and [(Me_4en)Pd(mvps)]$_2$(ClO_4)$_4$·2(Me_2CO)

	[(Me_4en)Pd(dmps)]$_2$(ClO_4)$_4$·2(Me_2CO)	[(Me_4en)Pd(mvps)]$_2$(ClO_4)$_4$·2(Me_2CO)
Formula	$C_{42}H_{72}N_8O_{18}Si_2Cl_4Pd_2$	$C_{44}H_{72}N_8O_{18}Si_2Cl_4Pd_2$
Weight	1387.86	1411.88
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*
a/Å	21.6932(6)	22.028(1)
b/Å	11.4005(3)	11.3444(6)
c/Å	24.5196(7)	24.907(1)
V/Å^3	6064.0(3)	6224.1(6)
Z	4	4
ρ/Mg m^{-3}	1.520	1.507
μ/mm^{-1}	0.879	0.858
F(000)	2848	2896
R_{int}	0.0896	0.0758
GOF on F^2	99.7% (θ = 26.50º)	99.6% (θ = 26.0º)
Final *R* [I>2σ(I)][a]	0.0530	0.0615
R (all data)[b]	0.1762	0.1789

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.



Scheme 1. Synthesis of $[(Me_4en)Pd(L)]_2(ClO_4)_4$ and hydrogenation catalysis.

NMR, and elemental analyses further supported the formation of the proposed complexes. The reaction was performed originally in the 1:1 mole ratio of Pd(II):L, but the products were not significantly affected by either the mole ratio or the concentration, indicating the metallacyclodimer is very favorable species. The products are soluble in acetone, methanol, acetonitrile, and dimethyl sulfoxide, but insoluble in chloroform, dichloromethane, and *n*-hexane. For the palladium(II) complexes, characteristic IR frequency of ClO_4^- anion appeared at 1089 cm^{-1} irrespective of L, indicating that the perchlorate acts as a counteranion rather than an anionic ligand. The other peaks of the IR spectrum remain virtually unchanged, suggesting that the cyclodimeric skeleton is retained.

Crystal Structures. All crystals as acetone solvate were obtained in an orthorhombic space group. The crystal structures of $[(Me_4en)Pd(L)]_2(ClO_4)_4$ are depicted in Figure 1, and relevant bond lengths and angles are listed in Table 2. The skeletal structure affords a 20-membered centrosymmetric cyclodimer. For the two complexes, the local geometry around the palladium(II) ion approximates to a typical square planar arrangement with two nitrogen atoms from Me_4en in a *cis* position (Pd-N = 2.054(4), 2.061(4) Å for $[(Me_4en)Pd(dmps)]_2(ClO_4)_4$; 2.070(5), 2.056(6) Å for $[(Me_4en)Pd(mvps)]_2(ClO_4)_4$; N-Pd-N = 85.9(2)° for $[(Me_4en)Pd(dmps)]_2(ClO_4)_4$; 85.8(2)° for $[(Me_4en)Pd(mvps)]_2(ClO_4)_4$) and two other nitrogen atoms from two pyridyl groups in a *cis* position (P-N = 2.037(4), 2.038(4) Å for $[(Me_4en)Pd(dmps)]_2(ClO_4)_4$; 2.033(5), 2.030(5) Å for $[(Me_4en)Pd(mvps)]_2(ClO_4)_4$; N-Pd-N = 87.0(2)° for $[(Me_4en)Pd(dmps)]_2(ClO_4)_4$; 86.0(2)° for $[(Me_4en)Pd(mvps)]_2(ClO_4)_4$) as well. L connects two palladium(II) ions to form a molecular rhombus with the Pd···Pd separations of 10.269(1) and 10.353(1) Å for $[(Me_4en)Pd(dmps)]_2(ClO_4)_4$ and $[(Me_4en)Pd(mvps)]_2(ClO_4)_4$, respectively, and Si···Si separations of 8.649(2) and 8.547(4) Å for $[(Me_4en)Pd(dmps)]_2(ClO_4)_4$ and $[(Me_4en)Pd(mvps)]_2(ClO_4)_4$, respectively. That is, the Pd···Pd distances are inversely proportional to the Si···Si distances. The pyridyl groups are walls of the macrocyclic rhombus. The ligand acts as a bent

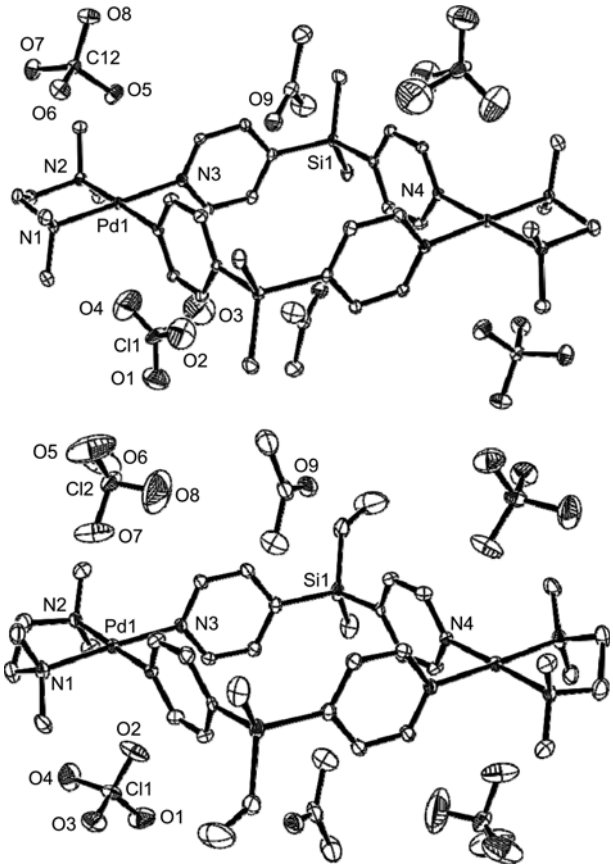


Figure 1. ORTEP drawings of $[(Me_4en)Pd(dmps)]_2(ClO_4)_4{\cdot}2(Me_2CO)$ (top) and $[(Me_4en)Pd(mvps)]_2(ClO_4)_4{\cdot}2(Me_2CO)$ (bottom) showing thermal ellipsoids at 20% probability. Hydrogen atoms were omitted for clarity.

bidentate (C-Si-C = 104.0(2)° for $[(Me_4en)Pd(dmps)]_2(ClO_4)_4$; 104.8(3)° for $[(Me_4en)Pd(mvps)]_2(ClO_4)_4$) tectonic, which is very useful in the construction of metallamacrocyclodimer. The formation of the discrete cyclodimer can be attributed to the hemicircle bidentate tectonic. The perchlorate anion acts as a counteranion rather than an anionic ligand (the shortest Pd···O distance = 3.333(6) Å for $[(Me_4en)Pd(dmps)]_2(ClO_4)_4$; 3.317(9) Å for $[(Me_4en)Pd(mvps)]_2(ClO_4)_4$). The solvate

Table 2. Selected bond lengths (Å) and angles (º) for $[(Me_4en)Pd(dmps)]_2(ClO_4)_4{\cdot}2(Me_2CO)$ and $[(Me_4en)Pd(mvps)]_2(ClO_4)_4{\cdot}2(Me_2CO)$

	$[(Me_4en)Pd(dmps)]_2(ClO_4)_4$	$[(Me_4en)Pd(mvps)]_2(ClO_4)_4$
Pd(1)–N(1)	2.061(4)	2.070(5)
Pd(1)–N(2)	2.054(4)	2.056(6)
Pd(1)–N(3)	2.037(4)	2.033(5)
Pd(1)–N(4)$^{\#1}$	2.038(4)	2.030(5)
Pd(1)···Pd(1)$^{\#1}$	10.269(1)	10.353(1)
Si(1)···Si(1)$^{\#1}$	8.649(2)	8.547(4)
Pd(1)···$OClO_3$	3.333(6)	3.317(9)
N(1)–Pd(1)–N(2)	85.9(2)	85.8(2)
N(3)–Pd(1)–N(4)$^{\#1}$	87.0(2)	86.0(2)
C(9)–Si(1)–C(12)	104.0(2)	104.8(3)

$^{\#1}$–x, –y+1, –z for $[(Me_4en)Pd(dmps)]_2(ClO_4)_4$; –x, 2–y, 2–z for $[(Me_4en)Pd(mvps)]_2(ClO_4)_4$

Table 3. Catalytic effects of $[(Me_4en)Pd(dmps)]_2(ClO_4)_4$ and $[(Me_4en)Pd(mvps)]_2(ClO_4)_4$ for hydrogenation

Entry	Substrate	Catalyst	Cat. mol %	H_2 pressure (psi)	Conv. (%)	TON[a]
1	Cyclohexene	$[(Me_4en)Pd(mvps)]_2(ClO_4)_4$	0.25	50	45.0	18,000
2	Cyclohexene	$[(Me_4en)Pd(dmps)]_2(ClO_4)_4$	0.25	50	18.5	7,400
3	1-Hexene	$[(Me_4en)Pd(dmps)]_2(ClO_4)_4$	0.25	50	100	40,000

[a]TON = tum over number

acetone molecules exist in up and down between counter-anions of a rhombus skeleton. No other exceptional features, neither those of bond lengths nor angles, were observed.

Cyclodimerization and Catalytic Effects. A combination of the square planar palladium(II) ion and the appropriate length and conformation of L is a significant factor for the formation of the metallacyclodimeric species. The skeleton was exclusively constructed irrespective of the mole ratio of the reactants, the solvent types, and the concentrations, reflecting that the cyclodimer is thermodynamically stable species. The less metallophilic perchlorate anion acts as a counteranion.[26] Even though this crystallization occurs in a mixed solvent, $[(Me_4en)Pd(L)]_2(ClO_4)_4$ selectively enclathrates only acetone, as shown in Figure 1. What is the critical driving force behind the acetone container? The acetone solvation seems to be attributed to the felicitous "size-influence" rather than the "specific non-covalent interaction" character.

In order to test the catalytic effects on hydrogenation of the metallacyclodimeric palladium(II) complexes, a preliminary test was achieved (Table 3): When hydrogen gases (50 psi) were bubbled into the *N,N*-dimethylformamide solution (10 mL) of cyclohexene (1 mL) or 1-hexene (1 mL) containing 0.25 mol % of the palladium(II) complexes (31.8 mg for $[(Me_4en)Pd(dmps)]_2(ClO_4)_4$; 32.4 mg for $[(Me_4en)Pd(mvps)]_2(ClO_4)_4$) as a homogeneous catalyst for 3 h, the substrate was hydrogenated. Thus, the yields of hydrogenation including other attempts are proportional to the quantity of the catalysts. The mechanism of the hydrogenation was considered to follow the common homogeneous hydrogenation process of palladium(II) compounds.[27] The hydrogenation was attempted in methanol, ethanol, and acetone, but the catalysts are insoluble or less soluble in the solvents. In particular, for the case of $[(Me_4en)Pd(mvps)]_2(ClO_4)_4$, the vinyl group was easily hydrogenated compared to the substrate (Supporting Information). Nevertheless, interesting difference in catalytic effects between $[(Me_4en)Pd(mvps)]_2(ClO_4)_4$ and $[(Me_4en)Pd(dmps)]_2(ClO_4)_4$ was observed: $[(Me_4en)Pd(mvps)]_2(ClO_4)_4$ is more effective than $[(Me_4en)Pd(dmps)]_2(ClO_4)_4$, indicating that various factors including electronic effect of alkyl group attached to silicon atom are involved in the hydrogenation. The catalysis using $[(Me_4en)Pd(dmps)]_2(ClO_4)_4$ was attempted for two substrates of cyclohexene and 1-hexene. 1-Hexene was completely converted into *n*-hexane whereas cyclohexene was partially converted into cyclohexane in 18.5%. Such a fact implies an important mechanistic aspect on the catalysis. That is, the steric hindrance of substrate is a significant factor for this hydrogenation. There is a temptation to invoke macrocyclic ring effect of the catalyst. The bulky Me_4en and perpendicular pyridyl groups are obstacles to substrate access, and alludes that the mode of action for the hydrogenation may occur through the macrocycle.

Attempt to recover the catalyst was carried out in order to confirm the behavior of the catalyst after hydrogenation reaction.[28] After hydrogenation reaction, the catalyst was separated by the addition of diethyl ether into the mixed solution, followed by simple filtration. Moreover, the IR and ^1H NMR spectra of the catalyst were unchanged after hydrogenation except for the vinyl moiety attached to the silicon atoms for $[(Me_4en)Pd(mvps)]_2(ClO_4)_4$. From these results it may be concluded that the catalyst remain practically unchanged after the hydrogenation reaction.

Conclusions

New ionic metallacyclodimeric palladium(II) complexes of silicon-containing pyridyl ligands were constructed and fully characterized. Delicate difference in catalytic effects based on the structures of catalysts and substrate was investigated. Such a macrocyclic system can contribute to recognize small molecules including anions. For the purposes of more effective rational control, more systematic studies including recognition of small organic molecules and catalysis, are in progress.

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Supporting Information. ^1H NMR spectra showing the catalytic effects on hydrogenation of $[(Me_4en)Pd(L)]_2(ClO_4)_4$. The informations are available on request from the correspondence author.

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