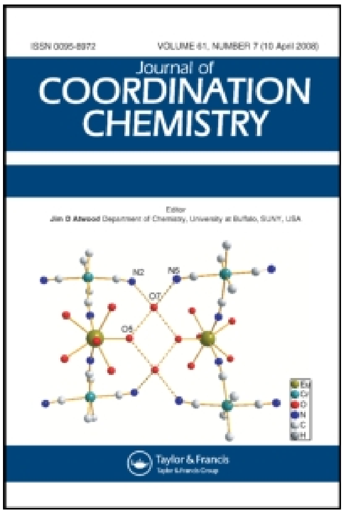

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
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Anion-recognition of an ionic cyclodimeric Pd(II) complex

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First published on: 11 October 2010

To cite this Article Ryu, Yoon Kyong , Kim, Chi Won , Noh, Tae Hwan , Yoo, Kyung Ho and Jung, Ok-Sang(2010) 'Anion-recognition of an ionic cyclodimeric Pd(II) complex', Journal of Coordination Chemistry, 63: 22, 3888 — 3896, First published on: 11 October 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.523825

URL: http://dx.doi.org/10.1080/00958972.2010.523825

Journal of Coordination Chemistry
Vol. 63, No. 22, 20 November 2010, 3888–3896

Anion-recognition of an ionic cyclodimeric Pd(II) complex

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(*Received 28 April 2010; in final form 26 August 2010*)

Ionic macrocyclodimeric palladium(II) complex, $[(\text{dppp})\text{Pd}(m\text{-pmps})]_2(\text{CF}_3\text{SO}_3)_4$ (dppp = 1,3-*bis*(diphenylphosphino)propane; *m*-pmps = 1,3-*bis*(3-pyridyl)-1,3-dimethyl-1,3-diphenyldisiloxane), was synthesized and its molecular structure determined by X-ray single crystallography. The complex has 19 rings consisting of one 20-membered metallamacrocycle, 2 six-membered metallacycles, 4 pyridyl groups, and 12 phenyl groups. The local geometry around palladium(II) approximates to a typical square planar arrangement with two *cis* phosphines (P–Pd–P = 90.54(7)°; N–Pd–N = 84.6(2)°; Pd–P = 2.259(2) Å, 2.270(2) Å; Pd–N = 2.100(5) Å, 2.112(5) Å). The triflates were smoothly exchanged to produce $[(\text{dppp})\text{Pd}(m\text{-pmps})]_2(\text{X})_4$ ($\text{X}^- = \text{NO}_3^-$, ClO_4^-, BF_4^-, PF_6^-, and SbF_6^-; $(\text{X})_2 = \text{SO}_4^{2-}$ and MoO_4^{2-}). According to ^{1}H-NMR chemical shifts and conductivity measurements, the macrocyclodimer was sensitive to the Hoffmeister series of anions.

Keywords: Anion-recognition; Crystal structure; Hoffmeister series; Metallacyclodimer

1. Introduction

Polyatomic anions such as nitrate, triflate, perchlorate, and hexafluorophosphate have become an emerging field owing to attention from the fields relating to environmental pollution, industrial, chemical, and biological processes, ionic liquids, catalysis, lithium battery, and health-related perspectives [1–7]. Recent developments include advances in anion template assembly, ion-pair recognition, and the function of anions in supramolecular chemistry [8–11]. Features of polyatomic anions such as negative charge, size, geometries, significant solvent effects, and pH dependence imply that the anions play crucial roles in molecular construction [12–14]. To recognize polyatomic anions, metal coordination receptors can be specifically designed according to basic components such as coordination geometry of the metal, binding site of the donating atoms, reactivity, charge, and the length of the spacer [2, 15]. Detection of polyatomic anions plays roles in multidisciplinary areas such as inorganic chemistry, environmental chemistry, sensing materials, and biomimicry [5, 16–18]. Our results have advanced [19–22] and various metallamacrocyclic complexes have constructed functional

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2010.523825

supramolecular materials utilized for molecular recognition, selective transformations, drug delivery systems, catalysts, storage, and biomimics [23–30]. Palladium(II)-macrocycles of multidentate *N*-donor ligands have contributed to catalysts [31], rectangle building blocks [32], submicrospheres [33], task-specific morphology [34], and magic rings with associative/dissociative dual character Pd–N bonds [35]. Preliminary results in an unusual anionic effect of dimeric palladium(II)-macrocyclic compounds containing 1,3-*bis*(3-pyridyl)tetramethyldisiloxane (*m*-ptms) have recently been published [36]. To further evaluate anion recognition of ionic palladium(II) macrocyclodimers, we report a new palladium(II) analogue containing 1,3-*bis*(3-pyridyl)-1,3-dimethyl-1,3-diphenyldisiloxane (*m*-pmps) along with its anion exchange. The *m*-pmps is a *N*-donor bipyridyl ligand containing 1,3-dimethyl-1,3-diphenyldisiloxane instead of tetramethyldisiloxane (*m*-ptms).

2. Experimental

2.1. *Materials and measurements*

Most chemicals including potassium tetrachloropalladate(II), 1,3-*bis*(diphenylphosphino)propane (dppp), silver trifluoromethanesulfonate, and *n*-butyllithium (Aldrich) and 1,3-dichloro-1,3-dimethyl-1,3-diphenyldisiloxane (Gelest) were used without purification. In this study, (dppp)$PdCl_2$ [37] and (dppp)$Pd(CF_3SO_3)_2$ [36] were prepared according to the procedure described in the literature. 1,3-*Bis*(3-pyridyl)-1,3-dimethyl-1,3-diphenyldisiloxane (*m*-pmps) was prepared according to the method given in our previous paper [38]. ^{1}H-NMR spectra were recorded on a Varian Mercury Plus 300 operating at 300.00 MHz and the chemical shifts were relative to internal Me_4Si. Infrared (IR) spectra were obtained on a Nicolet 380 fourier transform infrared spectroscopy (FTIR) spectrophotometer with samples prepared as KBr pellets. Conductivity was measured in acetonitrile using a Sartorius Professional Meter PP-50. Elemental microanalyses (C, H, and N) were performed on solid samples by the Pusan center, KBSI, using a Vario-EL III. Thermal analysis was performed under a nitrogen atmosphere at a scan rate of 10°C min^{-1} with a Labsys TGA-DSC 1600.

2.2. *Synthesis of [(dppp)Pd(m-pmps)]$_2$(CF_3SO_3)$_4$*

An acetone solution (2 mL) of *m*-pmps (4.13 mg, 0.01 mmol) was slowly diffused into an acetone solution (2 mL) of (dppp)$Pd(CF_3SO_3)_2$ (8.17 mg, 0.01 mmol). Slow evaporation of the solvent produced pale yellow crystals of [(dppp)Pd(*m*-pmps)]$_2(CF_3SO_3)_4$ in 80% yield (10.52 mg). Anal. Calcd for $C_{52}H_{64}N_2O_{10}F_6Si_2P_2S_2Pd$ ([(dppp)Pd(*m*-pmps)]$_2(CF_3SO_3)_4 \cdot 4Me_2CO$) (%): C, 52.66; H, 4.64; and N, 2.08. Found: C, 52.86; H, 4.80; and N, 2.11. IR (KBr, cm^{-1}): 1437, 1259 (s, $CF_3SO_3^-$), 1159, 1029, 837, 796, 638 ($CF_3SO_3^-$), and 515. ^{1}H-NMR (300 MHz, CD_3CN, ppm): $\delta = 8.49$ (s, 8H), 7.60–7.06 (s, 68H, overlapped protons of phenyl and pyridyl groups), 3.05 (br, 8H), 1.26 (s, 4H), and 0.54 (br, 12H).

Table 1. Crystal data and structure refinement for $[(dppp)Pd(m\text{-}pmps)]_2(CF_3SO_3)_4 \cdot 4Me_2CO$.

Empirical formula	$C_{118}H_{124}F_{12}N_4O_{18}Si_4P_4S_4Pd_2$
Formula weight	2691.49
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	15.854(3)
b	28.110(6)
c	15.731(3)
α	90
β	106.87(3)
γ	90
Volume (Å^3), Z	6709(2), 2
Calculated density (g cm^{-3})	1.332
Absorption coefficient (mm^{-1})	0.490
Completeness to $\theta = 26.00$ (%)	98.9
Data/restraints/parameters	13,050/6/750
Goodness-of-fit on F^2	1.064
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0838$, $wR_2 = 0.2485$
R indices (all data)	$R_1 = 0.1099$, $wR_2 = 0.2835$

$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = (\sum w(F_o^2 - F_c^2)^2/\sum wF_o^2)^{1/2}$.

2.3. *Anion exchange*

In this study, $[(dppp)Pd(m\text{-}pmps)]_2(X)_4$ ($X^- = NO_3^-$, ClO_4^-, BF_4^-, PF_6^-, and SbF_6^-; $(X)_2 = SO_4^{2-}$ and MoO_4^{2-}) were prepared by anion exchange of $[(dppp)Pd(m\text{-}pmps)]_2(CF_3SO_3)_4$ with the sodium salts of the anions in 1 : 10 molar ratio in water or a mixture of acetone : water. The anion exchange was monitored by anion IR bands and was completed within 2 h. Their chemical analyses, nuclear magnetic resonance (NMR), and IR spectra were satisfactory.

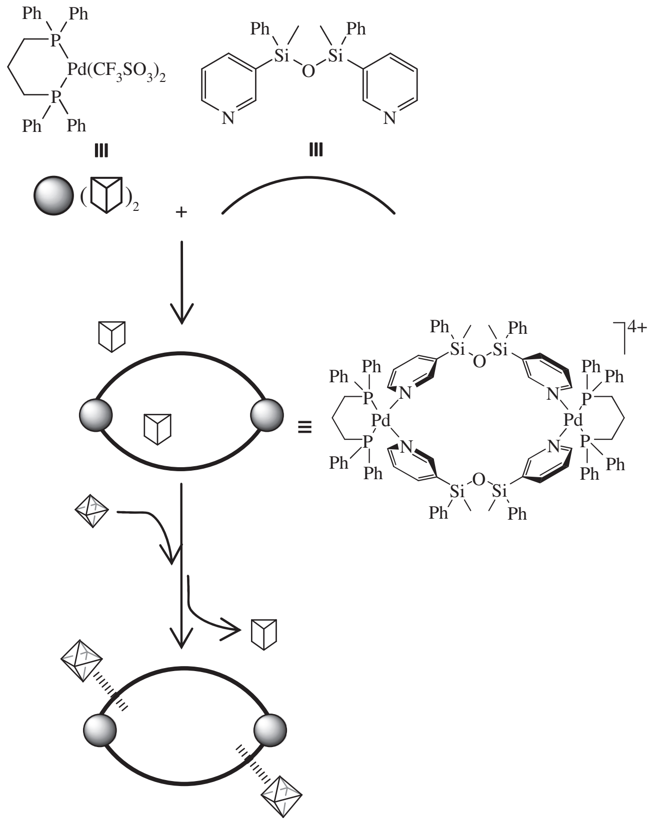
2.4. *Crystal structure determination*

X-ray data were collected on a Bruker SMART automatic diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and a CCD detector at 153 K. Thirty-six frames of two dimensional diffraction images were collected and processed to obtain cell parameters and orientation matrix. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected using the multi-scan method. The structures were solved using direct methods (*SHELXS-97*) and refined by full-matrix least squares (*SHELXL-97*) [39]. The non-hydrogen atoms were refined anisotropically and hydrogens were placed in calculated positions and refined only for the isotropic thermal factors. The crystal parameters and procedural information corresponding to data collection and structure refinement are listed in table 1.

3. Results and discussion

3.1. *Synthesis and characterizations*

Reaction of $(dppp)Pd(CF_3SO_3)_2$ with m-pmps in acetone at room temperature produced a discrete cyclodimeric species, $[(dppp)Pd(m\text{-}pmps)]_2(CF_3SO_3)_4$ in



Scheme 1. Schematic representation of the reaction.

high yield. The reaction was originally carried out in 1 : 1 mole ratio using *cis*-protected (dppp)Pd(CF_3SO_3)$_2$ and *m*-pmps, but the products were not significantly affected by either the mole ratio or the concentrations, indicating that the cyclodimer is thermodynamically stable. The counteranions of [(dppp)Pd(*m*-pmps)]$_2$(CF_3SO_3)$_4$ were smoothly exchanged by sodium salts of NO_3^-, ClO_4^-, BF_4^-, PF_6^-, and SbF_6^-, SO_4^{2-} and MoO_4^{2-} in 1 : 10 mole ratio in acetone or in a mixture of acetone/water, as shown in scheme 1. All products were obtained as stable solids soluble in acetonitrile, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and nitromethane, but insoluble in water, acetone, methanol, and ethanol. The elemental analyses, thermogravimetric analysis (TGA), and ^{1}H-NMR spectra were consistent with the proposed structures. IR frequencies of $CF_3SO_3^-$, PF_6^-, ClO_4^-, SbF_6^-, BF_4^-, NO_3^-, MoO_4^{2-}, and SO_4^{2-} were at 1281, 841, 1092, 733, 1092, 1383, 858, and 1252 cm^{-1}, respectively (Supplementary material).

3.2. *Crystal structure of [(dppp)Pd(m-pmps)]$_2$(CF_3SO_3)$_4$*

The crystal structure of pale yellow crystals of [(dppp)Pd (*m*-pmps)]$_2$(CF_3SO_3)$_4$ · 4Me_2CO was solved; selected bond lengths and angles are listed in table 2. The crystal structure depicted in figure 1 indicates that the molecule is a

Table 2. Relevant bond lengths (Å) and angles (°) of $[(dppp)Pd(m\text{-}pmps)]_2(CF_3SO_3)_4$.

Pd(1)–N(1)	2.100(5)
Pd(1)–N(2)$^{\#1}$	2.112(5)
Pd(1)–P(1)	2.259(2)
Pd(1)–P(2)	2.270(2)
N(1)–Pd(1)–N(2)$^{\#1}$	84.2(2)
N(1)–Pd(1)–P(1)	175.2(2)
N(2)$^{\#1}$–Pd(1)–P(1)	93.8(1)
N(1)–Pd(1)–P(2)	91.2(2)
N(2)$^{\#1}$–Pd(1)–P(2)	175.4(1)

$^{\#1}-x, -y+1, -z$.

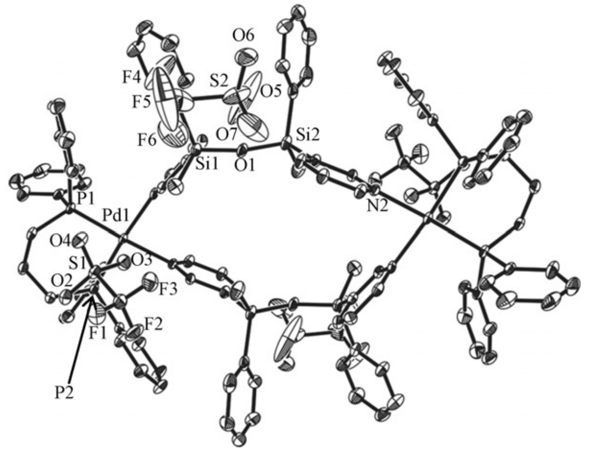


Figure 1. Oak Ridge Thermal Ellipsoid Plot Program (ORTEP) of $[(dppp)Pd(m\text{-}pmps)]_2(CF_3SO_3)_4 \cdot 4Me_2CO$ with thermal ellipsoids at the 30% level. Hydrogens and solvated molecules were omitted for clarity.

centrosymmetric cyclodimer. The local geometry around palladium approximates to a square planar arrangement with two *cis* phosphines (P–Pd–P = 90.54(7)°; N–Pd–N = 84.6(2)°; Pd–P = 2.259(2) Å, 2.270(2) Å; and Pd–N = 2.100(5) Å, 2.112(5) Å). The *m*-pmps connects two palladium(II) ions to form a 20-membered macrocyclodimer. The cyclodimeric complex has 19 rings with one 20-membered metallamacrocycle, two six-membered metallacycles, four pyridyl groups, and 12 phenyl groups. The ligand is a bidentate semicircle, useful in construction of metallamacrocyclodimers [29]. No exceptional features in bond lengths or angles were observed. The triflates are counteranions, not coordinated (the shortest Pd ··· O distance is 3.234(5) Å), and no anion is positioned inside the metallacycle. The dppp is *cis*-bidentate. The solvate acetone evaporates from 50–130°C (4.53%) and the skeletal structure begins to collapse at 294°C (Supplementary material).

3.3. *Conductivity*

Conductivity of the ionic cyclodimers in acetonitrile was measured to investigate the interactive properties of anions. The conductivity was measured at $3.0 \times 10^{-4}\,\mathrm{mmol\,L^{-1}}$

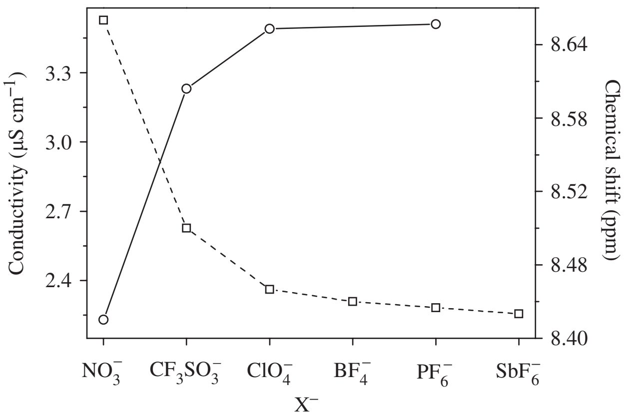


Figure 2. Conductivities (circle, solid line) and chemical shifts of pyridyl protons (square, dotted line) of $[(dppp)Pd(m\text{-}pmps)]_2(X)_4$.

at 23°C. The conductivity was in the order PF_6^- (3.51 μS cm^{-1}) > ClO_4^- (3.49 μS cm^{-1}) > $CF_3SO_3^-$ (3.23 μS cm^{-1}) > NO_3^- (2.23 μS cm^{-1}), as shown in figure 2. Unfortunately, BF_4^- and SbF_6^- analogs could not be measured due to their low solubility. The order is inversely proportional to the metallophilicity of the anions: the conductivity decreases as metallophilic nature increases. The Hoffmeister series of anions may be ordered as NO_3^- > $CF_3SO_3^-$ > ClO_4^- > PF_6^- [5, 21]. The diaionic MoO_4^{2-} and SO_4^{2-} analogs give 2.67 μS cm^{-1} and 2.77 μS cm^{-1}, respectively, at the same concentration. The conductivity of pure acetonitrile as a reference was 0.32 μS cm^{-1} at 23°C.

3.4. *^{1}H-NMR studies in solution*

^{1}H-NMR spectra of $[(dppp)Pd(m\text{-}pmps)]_2(X)_4$ ($X^- = NO_3^-$, $CF_3SO_3^-$, ClO_4^-, BF_4^-, PF_6^-, and SbF_6^-) were measured in CD_3CN at room temperature (figure 3). The ^{1}H-NMR signals are broad, presumably from the macrocyclic species containing bulky dppp. All complexes showed similar ^{1}H-NMR patterns, except for the chemical shifts of 2,6-H_2Py. The chemical shifts were deshielded in the order NO_3^- > $CF_3SO_3^-$ > ClO_4^-, BF_4^-, PF_6^-, SbF_6^-. Unfortunately, the order of ClO_4^-, BF_4^-, PF_6^-, and SbF_6^- could not be clearly discerned by NMR chemical shifts. The more metallophilic anions make the skeletal structure rigid even in solution, owing to the stronger anisotropy effect. For less metallophilic anions, the upfield shift of 2,6-H_2Py can be explained by additional fluxional motion of the pyridyl [40]. The 2,6-H_2Py chemical shifts of $[(dppp)Pd(m\text{-}pmps)]_2(X)_2$ ($X^{2-} = SO_4^{2-}$, MoO_4^{2-}) were similar to those of ClO_4^- analogs. However, direct comparison of the dianion complexes with the monoanion complexes is not easy owing to the different number of anions. Thus, the anions significantly affect the pyridyl groups rather than the phenyl of dppp. The phenyl groups are remote from the palladium(II), and thus not significantly affected. ^{1}H-NMR spectrum in $Me_2SO\text{-}d_6$ indicates that the structure is retained, but its chemical shifts are slightly shifted (Supplementary material: 8.59 ppm in $Me_2SO\text{-}d_6$; 8.50 ppm in CD_3CN). Thus, both ^{1}H-NMR and conductivity data give basic information on the interaction between the skeletal structure of the metal complex and the anion.

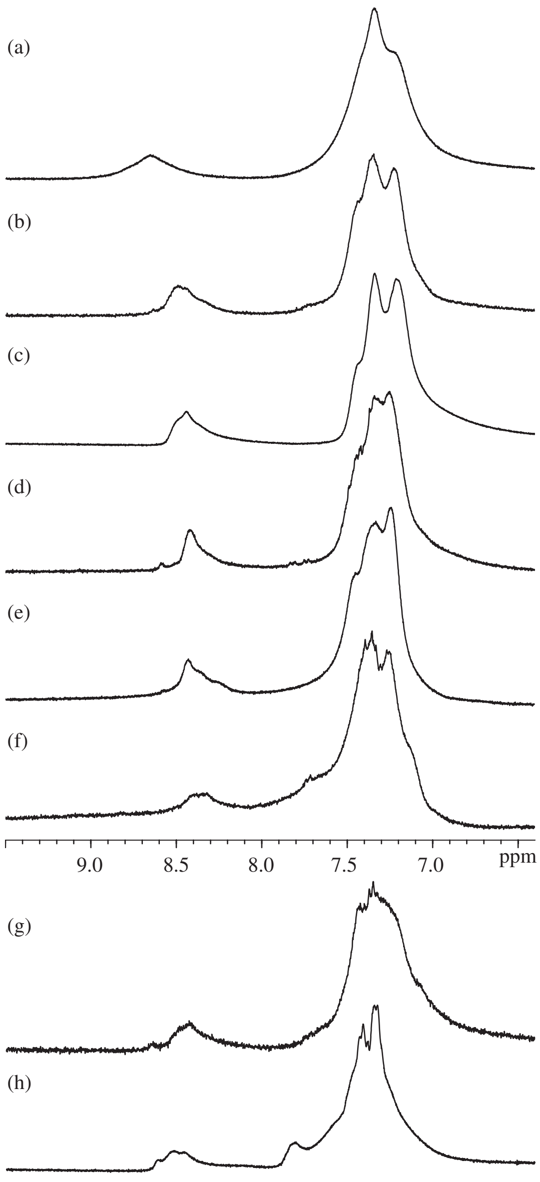


Figure 3. ^{1}H-NMR spectra of [(dppp)Pd(*m*-pmps)]$_2$(X)$_4$ in CD$_3$CN, $X^- = NO_3^-$ (a), $CF_3SO_3^-$ (b), ClO_4^- (c), BF_4^- (d), PF_6^- (e), SbF_6^- (f), $(X)_2 = SO_4^{2-}$ (g), and MoO_4^{2-} (h).

4. Conclusion

Metallacyclodimer was constructed and it is sensitive to metallophilicity of the polyatomic anion. These results contribute to the delicate modulation of metallacyclic receptors and anion-recognition, in addition to anion sensor, anion transport, and molecular switching.

Supplementary materials

IR spectra of [(dppp)Pd(*m*-pmps)]$_2$(X)$_4$, TGA data of [(dppp)Pd(*m*-pmps)]$_2$(CF_3SO_3)$_4$, ^{1}H-NMR spectra of [(dppp)Pd(*m*-pmps)]$_2$(CF_3SO_3)$_4$ in CD_3CN and in Me_2SO-d$_6$, and X-ray crystallographic data, in CIF format, for the structure determination of [(dppp)Pd(*m*-pmps)]$_2$(CF_3SO_3)$_4$ is deposited with the Cambridge Crystallographic Data Center, CCDC, under supplementary publication number CCDC-768361. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk].

Acknowledgments

This study was supported by a grant from the fundamental R&D program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

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