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Palladium Pincer Complexes with Reduced Bond Angle Strain: Efficient Catalysts for the Heck Reaction

Myeong Sik Yoon, Dowook Ryu, Jeongryul Kim, and Kyo Han Ahn*

Department of Chemistry, POSTECH, San 31 Hyoja-dong, Pohang 790-784, Republic of Korea

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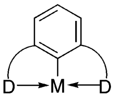
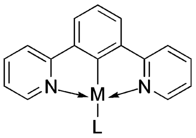
Summary: Palladium pincer complexes composed of six-membered fused metallacycles have been synthesized directly from 1,3-bis(2-pyridyloxy)benzene. The pincer complexes show remarkably high turnover numbers and frequencies in the Heck reaction.

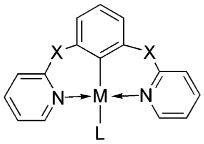
Organometallic complexes based on terdentate ligands containing a monoanionic aryl ligand, so-called pincer complexes, have been extensively studied as robust catalyst precursors in organic synthesis.[1] A typical type of pincer complexes is composed of a bicyclic, fused metallacycle in which the metal is coordinated by two donor heteroatoms (D) such as N, O, S, and P and a central anionic benzene ligand, in general depicted as **1**.



1



2



3

The pincer complexes developed so far usually have two five-membered fused metallacycles. During our study on the synthesis of chiral analogues of pincer complexes **2**,[2] we realized that this type of pincer complex would have rather severe bond angle strain around the metal center. A calculated structure at a semiempirical level for the chloropalladium complex **2a** (M = Pd, L = Cl)[3,4] suggested that the bond angles of C−Pd−N and N−Pd−Cl (82.51 and 97.49°, respectively) greatly deviate from the 90° that is expected for unstrained square-planar palladium complexes (Figure 1).[5]

Similarly, other pincer complexes similar to **2** are expected to have a certain degree of bond angle strain around the metal center. This bond angle strain may affect the catalytic properties of the pincer complexes. Therefore, it would be interesting to synthesize less strained pincer complexes and to evaluate their catalytic activity. To this end, we focused on pincer complexes of the type **3**. Insertion of "X" species such as O, S, and CH_2[6] between the central benzene and pyridine rings in **2** would decrease the bond angle strain around the metal center. The bond angle strain in such pincer complexes can be released by the conformational flexibility involving the heteroatom. In fact, in an energy-minimized structure of the chloropalladium complex **3a** (X = O, M = Pd, L = Cl), the bond angles C−Pd−N and N−Pd−Cl are 88.54 and 91.46°, respectively: values very close to 90°.[5] Thus, the pincer complex **3a** and its analogues seem to have little bond angle strain around the metal center, in which the two pyridine rings are not in plane but are twisted with respect to each other by about 48° (Figure 2).

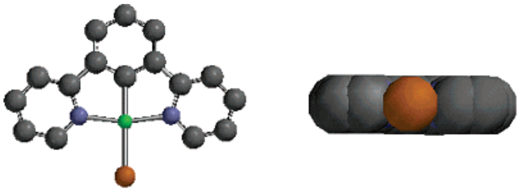


Figure 1. Modeled structure of pincer complex **2a** (M = Pd, L = Cl): top and side views.

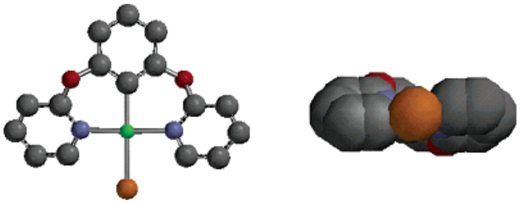


Figure 2. Calculated structure of pincer complex **3a** (X = O, M = Pd, L = Cl): top and side views.

Herein, we wish to report the synthesis of pincer complexes **3** and evaluation of their catalytic activity in the Heck reaction between aryl halides and methyl acrylate. We show that new pincer complexes composed of six-membered metallacycles show exceedingly high catalytic efficiency compared to that of the corresponding five-membered analogues.

Steel and co-workers reported that treatment of 1,3-bis(2-pyridyloxy)benzene (**4**) with $Pd(OAc)_2$ in acetic acid at room temperature did not give the pincer complex **3a** but rather gave an acetate-bridged cyclopalladated dimer, which was converted to the double-cyclopalladation compound **5**.[7] Interestingly, a similar cyclopalladation of 1,3-bis(2-pyridyloxy)naphthalene (**6**) in refluxing acetic acid resulted in the palladium pincer complex **7** (Scheme 1).[8] The catalytic activity of pincer complex **7** is not known.

A structural difference between the two ligands is that one of the three "CH" sites adjacent to the pyridyloxy groups is blocked by the fused benzene ring in the latter case. The formation of different complexes depending on the ligands'

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* To whom correspondence should be addressed. Tel: +82 54 279−2105. Fax: +82 54 279-3399. E-mail: ahn@postech.ac.kr.

[1] (a) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750−3781. (b) Singleton, J. T. *Tetrahedron* **2003**, *59*, 1837−1857.

[2] Ahn et al. Manuscript in preparation.

[3] Very recently, Soro et al. reported the synthesis of pincer complex **2a** (M = Pd; L = Cl) via a Hg(II) intermediate: Soro, B.; Stoccoro, S.; Minghetti, G.; Zucca, A.; Cinellu, M. A.; Gladiali, S.; Manassero, M.; Sansoni, M. *Organometallics* **2005**, *24*, 53−61.

[4] For the synthesis of a Pt(II) complex of **2** with K_2PtCl_4, see: Cárdenas, D. J.; Echavarren, A. M. *Organometallics* **1999**, *18*, 3337−3341.

[5] Molecular computations were performed using Spartan '04 Windows from Wavefunction, Inc.

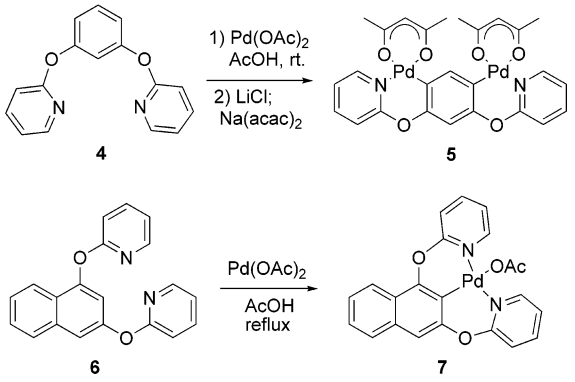
[6] A pincer complex that has X = CH(Me) has been reported, but its catalytic activity is not known; see: Canty, A. J.; Minchin, N. J.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1987**, 1477−1483.

[7] de Geest, D. J.; O'Keefe, B. J.; Steel, P. J. *J. Organomet. Chem.* **1999**, *579*, 97−105.

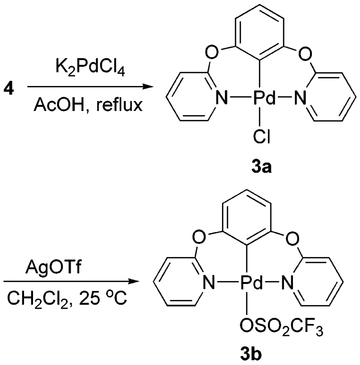
[8] O'Keefe, B. J.; Steel, P. J. *Organometallics* **2003**, *22*, 1281−1292.

10.1021/om0601246 CCC: $33.50

Scheme 1



Scheme 2



substitution pattern suggests that we may need 4- or 4,6-disubstituted derivatives of 1,3-bis(2-pyridyloxy)benzene to obtain their palladium pincer complexes.[9] Rather than pursuing this approach, we have investigated the synthesis of the palladium pincer complexes directly from ligand **4** simply by changing metal precursors. Attempts to synthesize palladium pincer complexes **3** by using palladium species such as $PdCl_2(CH_3CN)_2$, $PdCl_2(PPh_3)_2$, and $Pd(OAc)_2$/LiCl were not successful. Gratifyingly, the desired palladium pincer complex can be generated when K_2PdCl_4 is used as the metal source. Thus, treatment of **4** with K_2PdCl_4 in refluxing glacial acetic acid for 4 days afforded the pincer complex **3a** in 80% isolated yield (Scheme 2).

The chloropalladium complex **3a** thus obtained was converted to its triflate analogue **3b** by treating with silver triflate. The palladium species **3a** and **3b** were characterized by spectroscopic and mass analysis. The central benzene CH proton in **4** disappeared as pincer complex **3a** formed, together with concomitant chemical shift changes. Also, in the case of **3b**, apparent chemical shift changes were observed in comparison to the shifts for **3a**. Finally, a solid structure of the pincer complex **3b** was resolved by single-crystal X-ray crystallography (Figure 3),[10] which clearly shows that its molecular geometry is very similar to the calculated structure except for the triflate part. The solid structure of **3b** clearly shows that the two pyridine rings are out of the coordination plane and twisted 68.1° from each other. Also, the central phenyl plane is twisted 28.6° out of the coordination plane. The bond angles involving the metal center (88.2−92.0°) are close to 90°, which indicates that the bond angle strain around the metal center expected for the complex **2a** is released in our pincer complexes **3a** and **3b**.

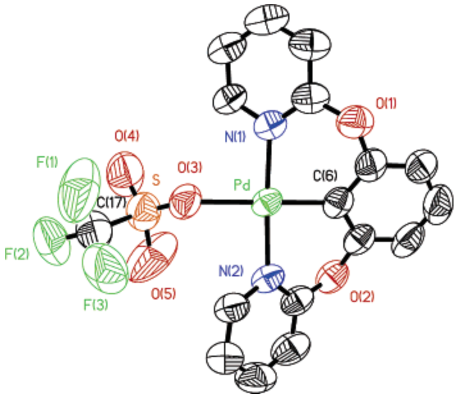
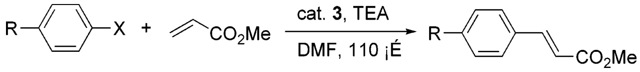


Figure 3. X-ray single-crystal structure of **3b**. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−C6 = 1.935, Pd−N1 = 2.047, Pd−N2 = 2.041, Pd−O3 = 2.187; C6−Pd−N1 = 88.2, C6−Pd−N2 = 88.4, O3−Pd−N1 = 91.5, O3−Pd−N2 = 92.0, N1−Pd−N2 = 176.5, C6−Pd−O3 = 178.5.

Table 1. Catalytic Activity of 3 in the Heck Reaction[a]



entry	catalyst (mol %)	R	X	yield (%)[b]	
				3b	**3a**
1	0.001	H	I	91	87
2	0.0001	H	I	82	
3	0.00001	H	I	53	
4	0.000001	H	I	34	
5	0.0000001	H	I	28	20
6	0.0000001	H	I	84[c]	43[c]
7	0.001	Me	I	96	
8	0.001	OMe	I	92	
9	0.001	Cl	I	84	
10	0.001	NO_2	I	91	
11	0.001	H	Br	14	*d*
12	0.001	Me	Br	37	
13	0.01	Me	Br	51	
14	0.001	NO_2	Br	54	
15	0.01	NO_2	Br	92	
16	0.1	CHO	Br	42	
17	0.1	NO_2	Cl	*d*	*d*

[a] Reaction conditions: 2.0 mmol of the halide substrate in DMF (10 mL), 3.0 mmol of methyl acrylate, 3.0 mmol of Et_3N, 14 h. [b] Isolated yield. [c] After 6 days. [d] No appreciable reaction.

The catalytic activity of pincer complexes **3** was evaluated in the Heck reaction between halobenzene derivatives and methyl acrylate in refluxing DMF in the presence of Et_3N.[11] Both the pincer complexes **3a** and **3b** are effective in the catalytic Heck reaction.[16] The results are summarized in Table 1. The complex **3b** was found to be more reactive than **3a**, giving higher coupling yields under the same reaction conditions. When we decreased the loading amount of **3b** from 10^{-3} to 10^{-7} mol % in the coupling reaction between 4-iodobenzene and methyl acrylate, the yield dropped from 91% to 28% under the given conditions (entries 1−5). However, we found that even under very dilute conditions in entry 5, the reaction still

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[9] Related Pd(II) and Ru(II) pincer complexes were formed with $Pd(OAc)_2$, but their catalytic activity data are not known; see: (a) Hartshorn, C. M.; Steel, P. J. *Organometallics* **1998**, *17*, 3487−3496. (b) Díez-Barra, E.; Guerra, J.; López-Solera, I.; Merino, S.; Rodríguez-López, J.; Sánchez-Verdú, P.; Tejeda, J. *Organometallics* **2003**, *22*, 541−547.

[10] Crystal data for **3b**: $C_{17}H_{11}F_3N_2O_5PdS$, $M_r = 518.74$, monoclinic, space group $P2_1/n$, $a = 24.040(8)$ Å, $b = 7.670(2)$ Å, $c = 11.429(4)$ Å, $V = 1853.9(10)$ Å^3, $Z = 4$, $T = 293(2)$ K, $\mu = 1.176$ mm^{-1}, 10 338 reflections collected, 3781 unique ($R_{int} = 0.0284$). Final R indices ($I > 2\sigma(I)$) (refinement on F^2): R1 = 0.0476, wR2 = 0.1385. For details, see the Supporting Information.

[11] Jung, I. G.; Son, S. U.; Park, K. H.; Chung, K.-C.; Lee, J. W.; Chung, Y. K. *Organometallics* **2003**, *22*, 4715−4720.

proceeded, and thus when we prolonged the reaction time to 6 days, the yield increased to 84% (entry 6). This result indicates that the pincer complex persists in the active form for 6 days in refluxing DMF. From these data, a remarkably high turnover number (TON = 8.4×10^8) and turnover frequency (TOF = 5.7×10^6 h^{-1}) are obtained. In the case of **3a**, both of the numbers obtained (TON = 4.3×10^8; TOF = 3.0×10^6 h^{-1}) greatly exceed those obtained with **2a** (TON = 7.5×10^4; TOF = 5.4×10^3 h^{-1}) under otherwise identical reaction conditions.[3] Thus, we have demonstrated that pincer complexes based on the six-membered metallacycles are much more efficient as catalyst precursors in the Heck reaction compared to the corresponding pincer complexes based on five-membered analogues. Although large TON values are observed in the Heck reaction with palladium pincer complexes or palladacycles as catalyst precursors,[12] as far as we know, the TON value obtained with **3b** is the highest value observed so far.[13] Further study is necessary to address the reasons our pincer complexes give such a large TON value compared to other pincer complexes.[14] It should be pointed out that the Heck reaction mechanism in the case of such pincer complexes is a point of controversy: that is, between the established Pd(0)/Pd(II) and new Pd(II)/Pd(IV) cycle.[12a,15] In any case, the robustness of pincer complexes **3** is likely due to the reduced bond angle strain, as we intended in its design, and this robustness should contribute to the enhanced TON values observed.

The coupling reaction with **3b** proceeded in good yields (84−96%) for other iodobenzene derivatives with electron-donating or -withdrawing substituents (entries 7−10 in Table 1). However, the reaction became slower when bromobenzene derivatives were used under the same conditions (entries 11−15) and little progress was observed in the case of chlorobenzene (entry 16).

In conclusion, we have synthesized novel Pd(II) pincer complexes of 1,3-bis(2-pyridyloxy)benzene by direct cyclopalladation with K_2PdCl_4 as the metal source. Our Pd(II) pincer complexes are composed of two six-membered fused palladacycles and have reduced bond angle strain around the metal center. An X-ray crystal structure was resolved for one of the palladium pincer complexes, which shows little bond angle distortion around the metal center. Our palladium pincer complexes show exceedingly high turnover number and frequency compared to those obtained with a five-membered metallacycle analogue. The catalytic efficiency observed is comparable to or exceeds the highest values obtained by related pincer complexes. Application of the pincer complexes to other catalytic reactions as well as their structural modification is under active investigation.

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Supporting Information Available: Text and figures giving details of the syntheses and characterization data of **3a** and **3b**, including their ^1H and ^{13}C NMR spectra, and a CIF file giving crystallographic data for **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0601246

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[12] (a) Herrmann, W. A.; Brossmer, C.; Öfele, K.; Reisinger, C.-P.; Priermeier, T.; Beller, M.; Fischer, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1844−1848. (b) Beller, M.; Fischer, H.; Herrmann, W. A.; Öfele, K.; Brossmer, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1848−1849. (c) Ohff, M.; Ohff, A.; van der Boom, M. E.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 11687−11688. (d) Miyazaki, F.; Yamaguchi, K.; Shibasaki, M. *Tetrahedron Lett.* **1999**, *40*, 7379−7383. (e) Ohff, M.; Ohff, A.; Milstein, D. J. *Chem. Commun.* **1999**, 357−358.

[13] A similar level of TON was reported, but at higher temperature (in refluxing NMP, 140 °C); see: Takenaka, K.; Uozumi, Y. *Adv. Synth. Catal.* **2004**, *346*, 1693−1696.

[14] A reviewer commented that the increased flexibility of our pincer complexes may facilitate the dissociation of one of the pyridine rings to generate a more coordinatively unsaturated and active catalyst system. Also, the O-atom linkers would make the phenyl ring a stronger σ-donor to the metal, which in turn might increase the potentially rate determining oxidative addition step. These explanations are based on the proposition that the Heck reaction by these pincer complexes follows the Pd(0)/Pd(II) mechanism.

[15] (a) Shaw, B. L. *New J. Chem.* **1998**, 77−79. (b) Herrmann, W. A.; Brossmer, C.; Reisinger, C.-P.; Riermeier, T. H.; Öfele, K.; Beller, M. *Chem. Eur. J.* **1997**, *3*, 1357−1364. (c) Herrmann, W. A.; Böhm, V. P. W.; Reisinger, C.-P. *J. Organomet. Chem.* **1999**, *576*, 23−41.

[16] Typical Heck reaction procedure: in a 25 mL Schlenk flask were added pincer complex **3b** (0.001%), triethylamine (0.42 mL, 3.0 mmol), iodobenzene (2.0 mmol), methyl acrylate (0.27 mL, 3.0 mmol), and DMF (10 mL), and the resulting mixture was refluxed (110 °C) in an oil bath for 14 h. The product was isolated by extractive workup with CH_2Cl_2 followed by flash column chromatography on silica gel (12/1 hexane/diethyl ether).