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Syntheses and Characterization of Palladium(II) Complexes with Tridentate N-Heterocyclic Carbene Ligands Containing Aryloxy Groups and Their Application to Heck Reaction

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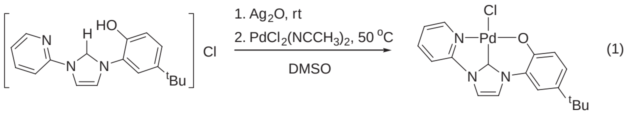
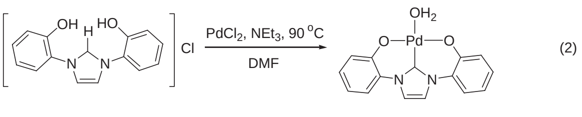
Two palladium(II) complexes with tridentate N-heterocyclic carbene ligands containing aryloxy groups were prepared and characterized by X-ray crystallographic method. They showed good performance for Heck reaction.

Transition-metal complexes with N-heterocyclic carbene ligands are of interest because of the high catalytic activity and stability compared with those with phosphine ones.[1] In order to investigate the activity and stability of carbene complexes, various carbene ligands such as pincer,[2] macrocycle,[3] tripod,[4] and multidentate ligand consisting of the carbene carbon and oxygen[5] or phosphine[6] as donor atoms have been prepared. Although the pincer ligands are known to give the stable complexes, there has been only one report for the complexes with pincer carbene ligands containing aryloxy groups.[5b] To accomplish high catalytic activity and thermal stability for palladium(II) complexes, we have designed new pincer complexes containing aryloxy substituents for the redox character[7] and negative charge of the ligands. There has been only one report on the palladium complexes with bidentate carbene ligands containing aryloxy groups, but catalytic activity of these complexes was not discussed.[5c] Two imidazolium salts, containing aryloxy and/or pyridine, were prepared as precursors for carbene compounds. In this paper, we describe the preparation of new palladium(II) complexes with pincer-type tridentate carbene ligands, the characterization of the structures using X-ray crystallographic methods and the catalytic property of the complexes for Heck reactions.



H$_2$L1Cl 1



H$_3$L2Cl 2

Imidazolium salts, 1-(2′-hydroxy-5′-*tert*-butylphenyl)-3-(2″-pyridyl)imidazolium chloride (H$_2$L1Cl), was prepared by the reaction of 2-chloropyridine with 1-(2′-hydroxy-5′-*tert*-butylphenyl)imidazole for 2 days at 150 °C. 1,3-Bis(2′-hydroxyphenyl)imidazolium chloride (H$_3$L2Cl) was prepared from *o*-aminophenol, glyoxal, formic acid, and paraformaldehyde according to the reported method for 1,3-bis(2′,6′-diisopropylphenyl)imidazolium salts.[8] Corresponding palladium(II) complexes, [Pd(L1)Cl] (**1**)[9] and [Pd(L2)(OH$_2$)] (**2**),[10] were prepared by the eqs 1 and 2, respectively. Figure 1 shows the crystal structures for **1** and **2**, which have distorted square-planar palladium centers.[11] L1 and L2 acted as tridentate ligands, where pyridyl nitrogen, carbene carbon, and aryloxy oxygen atoms bonded to the metal centers. It should be noted that the distances of the Pd–C bonds for both complexes (1.880(7) Å for **1** and 1.897(5) Å for **2**) were shorter than those for other carbene complexes previously reported (1.953(5)–2.004(3) Å).[5c,5d,12,13] The shortest Pd–C distances to our knowledge might be caused by the rigid structure of the tridentate ligands. Other distances of Pd–N and Pd–Cl bonds for **1** and **2** were similar values for the palladium(II) carbene complexes.[13] The ^{1}H NMR spectra of both complexes in DMSO-d_6 solution demonstrated complexation shifts and disappearance of hydroxy and imidazolium protons, indicating that the coordination structures of **1** and **2** observed in solution were similar to those in crystal phase. These complexes were stable in solid state and in solutions under aerobic condition for months at room temperature. Furthermore, complex **1** was stable for 24 h at 150 °C in dimethylacetamide (DMA).

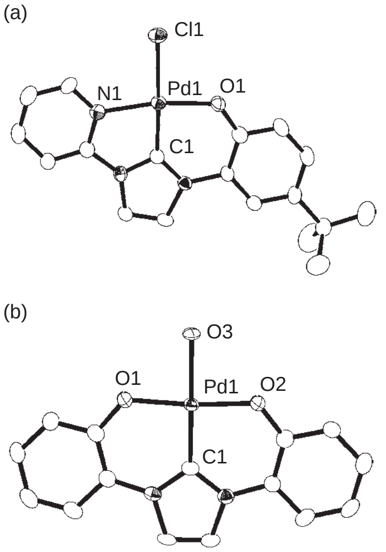
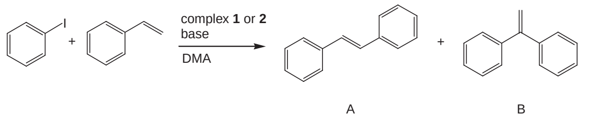


Figure 1. ORTEP drawing of **1** (a) and **2** (b) (50% probability). Selected bond lengths (Å) and angles (°) for **1**: Pd1–C1 1.880(7), Pd1–O1 1.990(5), Pd1–N1 2.054(6), Pd1–Cl1 2.377(2), O1–Pd1–N1 168.9(2), Cl1–Pd1–N1 177.6(2), Cl1–Pd1–N1 98.1(2), Cl1–Pd1–O1 93.0(1), O1–Pd1–C1 89.2(2), N1–Pd1–C1 79.7(3). Selected bond lengths (Å) and angles (°) for **2**: Pd1–C1 1.897(5), Pd1–O1 1.984(4), Pd1–O2 1.981(4), Pd1–O3 2.112(4), O1–Pd1–O2 174.4(2), O1–Pd1–O3 86.4(2), O1–Pd1–C1 93.0(2), O2–Pd1–O3 88.0(2), O2–Pd1–C1 92.6(2), O3–Pd1–C1 179.0(2).

Table 1. Heck coupling reactions of iodobenzene with styrene[a]

Entry	Catalyst	Amount/mol %	Base	T/°C	Time/h	Yield/%[b]	TON	Ratio of A:B[d]
1	**1**	2.0×10^{-1}	Cs_2CO_3	150	6	99	495	89:11
2	**1**	2.0×10^{-1}	NEt_3	110	6	99	495	89:11
3	**2**	2.0×10^{-1}	Cs_2CO_3	150	2	74[c]	370	88:12
4	**2**	2.0×10^{-1}	NEt_3	110	8	97	485	90:10
5	**1**	2.0×10^{-2}	NEt_3	110	8	90	4500	88:12
6	**1**	2.0×10^{-3}	NEt_3	110	20	96	48000	88:12
7	**1**	2.0×10^{-4}	NEt_3	110	48	27	135000	88:12

[a]Reactions were carried out with 2.0 mmol of iodobenzene, 2.8 mmol of styrene, and 2.2 mmol of base in 5 mL of DMA. [b]Total yield for A and B determined by GC. [c]Yield for 6 h was also 74%. [d]Determined by GC.



(3)

The catalytic activities for complexes **1** and **2** were investigated in the Heck reactions of iodobenzene with styrene in DMA as illustrated in eq 3. The reactions were carried out at 110 °C, while Entries 1 and 3 were investigated at higher temperature because of incomplete dissolution of Cs_2CO_3 in DMA. As summarized in Table 1, reaction products were *trans*-stilbene (A) and 1,1-diphenylethylene (B), of which ratio was about 9:1.[14] The reactions catalyzed by complex **1** proceeded quantitatively at both 150 and 110 °C (Entries 1 and 2). In the case of complex **2** (Entry 4), slightly longer reaction time was necessary for the reaction completed at 110 °C. On the other hand, the lower yield of the reaction products in Entry 3 is interpreted by the decomposition of the complex at 150 °C. These findings might indicate that complex **1** having five- and six-membered chelate rings showed higher thermal stability and catalytic activity than **2**. In addition, **1** also showed good catalytic performance; the turnover number (TON) of 135,000 is comparable to those for other pincer carbene complexes (Entries 5–7).[2a,2c] This high TON signifies that new tridentate carbene ligand containing aryloxy group plays an important role for stabilization and activation of palladium complex.

In summary, we prepared and characterized two new palladium(II) complexes with the pincer-type tridentate carbene ligands. The high catalytic activity for Heck reaction might be caused by the thermal stability of the palladium complex with rigid pincer-type ligand, in which the short Pd–C bond distance is important.

References and Notes

1 W. A. Herrmann, *Angew. Chem., Int. Ed.* **2002**, *41*, 1290; A. C. Hillier, G. A. Grasa, M. S. Viciu, H. M. Lee, C. Yang, S. P. Nolan, *J. Organomet. Chem.* **2002**, *653*, 69.

2 a) E. Peris, J. A. Loch, J. Mata, R. H. Crabtree, *Chem. Commun.* **2001**, 201. b) S. Gründemann, M. Albrecht, J. A. Loch, J. W. Faller, R. H. Crabtree, *Organometallics* **2001**, *20*, 5485. c) J. A. Loch, M. Albrecht, E. Peris, J. Mata, J. W. Faller, R. H. Crabtree, *Organometallics* **2002**, *21*, 700. d) A. M. Magill, D. S. McGuinness, K. J. Cavell, G. J. P. Britovsek, V. C. Gibson, A. J. P. White, D. J. Williams, A. H. White, B. W. Skelton, *J. Organomet. Chem.* **2001**, *617–618*, 546.

3 M. V. Baker, B. W. Skelton, A. H. White, C. C. Williams, *Organometallics* **2002**, *21*, 2674.

4 X. Hu, I. Castro-Rodriguez, K. Meyer, *J. Am. Chem. Soc.* **2003**, *125*, 12237; E. Mas-Marzá, M. Poyatos, M. Sanaú, E. Peris, *Organometallics* **2004**, *23*, 323.

5 a) J. J. Van Veldhuizen, S. B. Garber, J. S. Kingsbury, A. H. Hoveyda, *J. Am. Chem. Soc.* **2002**, *124*, 4954. b) H. Aihara, T. Matsuo, H. Kawaguchi, *Chem. Commun.* **2003**, 2204. c) A. W. Waltman, R. H. Grubbs, *Organometallics* **2004**, *23*, 3105. d) B. E. Ketz, A. P. Cole, R. M. Waymouth, *Organometallics* **2004**, *23*, 2835.

6 C. Yang, H. M. Lee, S. P. Nolan, *Org. Lett.* **2001**, *3*, 1511; N. Tsoureas, A. A. Danopoulos, A. A. D. Tulloch, M. E. Light, *Organometallics* **2003**, *22*, 4750.

7 S. Kimura, E. Bill, E. Bothe, T. Weyhermüller, K. Wieghardt, *J. Am. Chem. Soc.* **2001**, *123*, 6025; L. Benisvy, E. Bill, A. J. Blake, D. Collison, E. S. Davies, C. D. Garner, C. I. Guindy, E. J. L. McInnes, G. McArdle, J. McMaster, C. Wilson, J. Wolowska, *Dalton Trans.* **2004**, 3647.

8 L. Jafarpour, E. D. Stevens, S. P. Nolan, *J. Organomet. Chem.* **2000**, *606*, 49.

9 Anal. for $C_{18}H_{18}ClN_3OPd$: Found C 49.39, H 4.22, N 9.34, Calcd. C 49.79, H 4.18, N 9.68.

10 Anal. for $C_{15}H_{12}N_2O_3Pd$: Found C 47.75, H 3.19, N 7.18, Calcd C 48.08, H 3.22, N 7.48.

11 Crystal data for **1**: single crystals contain a MeOH molecule in an asymmetric unit; $C_{19}H_{22}ClN_3O_2Pd$, MW 466.25, monoclinic, $C2/c$ (No. 15), $a = 28.766(2)$ Å, $b = 9.4846(4)$ Å, $c = 14.8720(7)$ Å, $\beta = 104.450(2)°$, $V = 3929.2(3)$ Å^3, $Z = 8$, $T = 173$ K, $D_{calcd} = 1.576$ g/cm^3, total reflections = 15901, unique reflections = 4484, $R_1 = 0.053$, $R_w = 0.155$. Crystal data for **2**: $C_{15}H_{12}N_2O_3Pd$, MW 374.67, orthorhombic, $P2_12_12_1$ (No. 19), $a = 6.828(3)$ Å, $b = 12.274(5)$ Å, $c = 15.206(7)$ Å, $V = 1274.4(10)$ Å^3, $Z = 4$, $T = 173$ K, $D_{calcd} = 1.953$ g/cm^3, total reflections = 10260, unique reflections = 1690, $R_1 = 0.029$, $R_w = 0.072$. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

12 W. A. Herrmann, J. Schwarz, M. G. Gardiner, *Organometallics* **1999**, *18*, 4082; H. M. Lee, C. Y. Lu, C. Y. Chen, W. L. Chen, H. C. Lin, P. L. Chiu, P. Y. Cheng, *Tetrahedron* **2004**, *60*, 5807.

13 D. J. Nielsen, K. J. Cavell, B. W. Skelton, A. H. White, *Inorg. Chim. Acta* **2002**, *327*, 116; S. Gründemann, M. Albrecht, A. Kovacevic, J. W. Faller, R. H. Crabtree, *J. Chem. Soc., Dalton Trans.* **2002**, 2163; A. Füerstner, G. Seidel, D. Kremzow, C. W. Lehmann, *Organometallics* **2003**, *22*, 907; A. A. Danopoulos, A. A. D. Tulloch, S. Winston, G. Eastham, M. B. Hursthouse, *Dalton Trans.* **2003**, 1009; L. G. Bonnet, R. E. Douthwaite, R. Hodgson, *Organometallics* **2003**, *22*, 4384.

14 Preliminary study for Heck reaction of bromobenzene with styrene gave a yield of 36% for 24 h at 110 °C.

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