

A Highly Substitutable Palladium(II) Complex Stabilized by the Smallest Steric *N*-Heterocyclic Carbene, *IMe* (*IMe* = 1,3-Dimethylimidazole-2-ylidene)

Eunsung Lee,^{†,‡,§,*} Dae Young Bae,^{‡,§} and Dmitry V. Yandulov[†]

[†]Department of Chemistry, Stanford University, Stanford, CA, 94305-5080, USA. *E-mail: eslee@postech.ac.kr

[‡]Center for Self-assembly and Complexity (CSC), Institute for Basic Science (IBS), Pohang 790-784, Republic of Korea

[§]Department of Chemistry and Division of Advanced Materials Science, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea

Received September 1, 2016, Accepted September 21, 2016, Published online October 26, 2016

Keywords: Palladium, *N*-heterocyclic carbene, Monodentate, Labile ligand, Isomerization

Palladium complexes supported by *N*-heterocyclic carbenes (NHCs) have been of great interests in catalysis because of their capability as efficient catalysts in organic synthesis.^{1,2} Since the strong palladium–NHC bonds retain the stability of palladium complexes, and steric modification of the NHC ligands can be readily available, NHCs become more popular and important alternatives to phosphines as supporting ligands.^{3,4} Thus, the synthetic direction of NHCs has been aimed to optimize both electronic and steric properties of NHCs, which allows one to maximize the reactivity of inorganic catalysts for desired results.⁴ As the results, numerous Pd(II)–NHC complexes have been synthesized and applied in cross-coupling reactions, telomerization reactions, oxidation reactions including a catalytic conversion of methane to methanol.^{5–9} Although significant efforts have been made to increase steric bulkiness of NHC in particular,¹⁰ another simple approach to access a reactive palladium complex is to introduce labile ligands to a metal center. In addition, since mono-ligated palladium complexes have been also known as active catalysts in most palladium catalyzed organic reactions, efficient methods to generate mono-ligated NHC palladium complexes have been successfully developed and utilized for the organic synthesis.^{3,11}

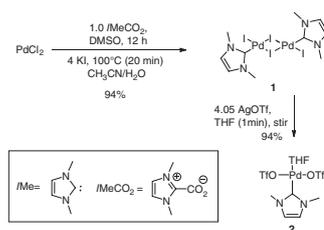
However, most of mono-ligated NHC palladium complexes contain bulky NHCs with relatively strongly bound anions such as acetate anions, or halide- or carboxylate-bridged palladium dimers are obtained.^{12,13} With weakly bound anions, the metalation of bulky NHC ligands has been observed in many cases and resulted in the deterioration of the palladium–NHC complexes.¹⁴ Therefore, the access to a mono-ligated NHC complex with weakly coordinating ligands is very limited.^{15,16} To overcome the problematic metalation of NHC, we have utilized the smallest steric NHC and successfully prepared mono-ligated palladium(II) complex with a weakly coordinating anion and tetrahydrofuran (THF).^{17,18} Here, we report the preparation and full characterization of a mono-ligated palladium(II) complex supported by *IMe* (*IMe* = 1,3-dimethylimidazole-2-ylidene), triflate, and THF.

Synthesis of Pd(*IMe*)(OTf)₂(THF) (**2**) complex involves the formation of iodo-bridged palladium(II) dimer (**1**),¹⁹

followed by halide abstraction of **1** with silver triflate in THF. Both complexes were obtained in 94% yield (Scheme 1). In the process of formation of **2**, iodide abstraction should be carried out within 1 min, followed by a quick filtration of the reaction mixture through a pad of Celite. Otherwise cationic polymerization of THF starts immediately, indicating strong interaction between THF and a highly naked palladium(II) center due to labile ligands. Addition of pentane to the filtrate affords immediately crystalline yellow **2**, which is further collected on a frit. Unlike most known stable palladium(II) NHC complexes in a solid phase, **2** decomposes to a black tar solid even at 50°C under dynamic vacuum, as the stability of **2** is not secured because of three labile ligands. However, the same approach to access the naked palladium complexes was not successful with sterically bulky NHCs such as 1,3-bis-(2,6-diisopropylphenyl)imidazolyliene (*IPr*)²⁰ and 1,3-di-*tert*-butylimidazole-2-ylidene (*t*Bu)¹⁹ because metalation of proximate C–H bonds in NHCs via the palladium metal ion results in decomposition of the complexes, as confirmed by ¹H NMR spectra.¹⁴ Such an undesired metalation was not observed with *IMe* because C–H bonds in the methyl group stay away from the naked palladium of **2**.

Single crystal X-ray analysis of a yellow crystal of **2** reveals that one THF molecule is coordinated to a Pd center at a *trans* position of *IMe* and two triflate anions are coordinated to the Pd center in a *trans* position, allowing a square planar conformation (Figure 1). The Pd – O_{THF} and Pd – O_{OTf} bond distances in the solid state are 2.119(6) and 2.032(2) Å and Pd – C_{IMe} bond distance is 1.938(4) Å. In a previously reported palladium(II) complex having both THF and NHC, the bulky di-*tert*-butyl substituents of the NHC and *trans* effect of η³-allyl ligand in the complex appears to elongate Pd – C_{NHC} bond distance to 2.064 Å.¹⁶ The theoretically computed structure of **2** is also in good agreement with above distances except the configuration of auxiliary ligands. The discrepancy of the ligand configuration may cause the weak coordination bonds.

As the palladium(II) complex **2** shows a low thermal stability, we investigated its electronic properties at the B3PW91/BS I level utilizing the Gaussian program (see Appendix S1,



Scheme 1. Synthesis of Pd(Ime)(OTf)₂(THF) (**2**) complex.

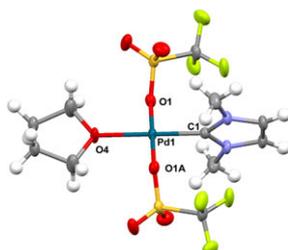


Figure 1. X-ray crystal structure of **2**. Selected experimental [calculated at the B3PW91/BS I level for the optimized structure] bond lengths [Å]. Pd1–C1 1.938(4) [1.943], Pd1–O1(O1A) 2.032(2) [2.034 and 2.039], Pd1–O4 2.119(6) [2.129].

Supporting information).²¹ Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of **2** are assigned to d_{xy} and $d_{x^2-y^2}$ orbitals of palladium, respectively, as typical d orbital configurations of a square planar palladium ion. None of HOMO and HOMO-1 shows π interaction between palladium and ligands because of the lack of available empty p orbitals in the ligands having the same symmetry with d orbitals of palladium (Figure 2). Only sigma bonding orbitals from ligands participate in metal–ligand coordination, as Ime is the only strong sigma donor. Therefore, triflate anions and THF in **2** can easily dissociate, which enables facile substitution with other ligands. Currently, we are investigating various ligand substitution reactivity of **2** is in progress along with discovering an interesting reactivity with **2**. For example, **2** is found as an efficient catalyst for isomerization of allylbenzene to *trans*- β -methylstyrene (see Appendix S1 and Scheme 2).

In summary, we have successfully synthesized mono-ligated NHC palladium(II) complex with a smallest steric NHC and three labile ligands. A key for the successful preparation of Pd(Ime)(OTf)₂(THF) (**2**) is to utilize Ime as a supporting

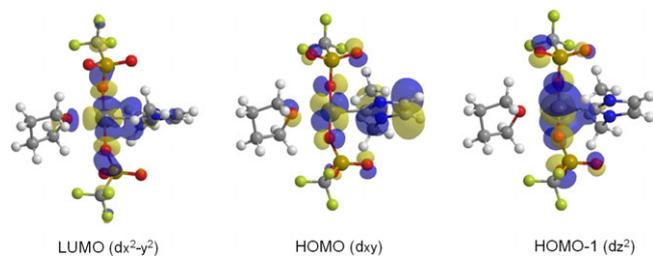
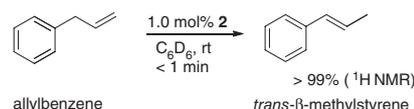


Figure 2. Molecular orbitals (LUMO, HOMO, HOMO-1) of **2** computed by B3PW91/BS I (isocontour = 0.3). There is a weak bonding between THF and Pd.



Scheme 2. Isomerization of allylbenzene to *trans*- β -methylstyrene catalyzed by **2**.

ligand because there is no adjacent C–H bond nearby palladium center, which is vulnerable to metalation. Thus, a highly substitutable and naked palladium(II) complex with one NHC could be isolated. We believe that the present palladium(II) complex can offer a potential application as an efficient catalyst for various organic reactions, which are in progress in our lab.

Acknowledgments. This work was supported by Stanford University and Institute for Basic Science (IBS) (IBS-R007-D1). We thank Dr Victor G. Young, Jr. for X-ray analysis.

Supporting Information. Details for experimental, X-ray and DFT data are available in the online version of this article.

References

- N. Marion, S. P. Nolan, *Acc. Chem. Res.* **2008**, *41*, 1440.
- G. C. Fortman, S. P. Nolan, *Chem. Soc. Rev.* **2011**, *40*, 5151.
- E. A. Kantchev, C. J. O'Brien, M. G. Organ, *Angew. Chem. Int. Ed. Engl.* **2007**, *46*, 2768.
- M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485.
- W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2371.
- J. A. Loch, M. Albrecht, E. Peris, J. Mata, J. W. Faller, R. H. Crabtree, *Organometallics* **2002**, *21*, 700.
- K. Selvakumar, A. Zapf, M. Beller, *Org. Lett.* **2002**, *4*, 3031.
- O. Navarro, R. A. Kelly 3rd., S. P. Nolan, *J. Am. Chem. Soc.* **2003**, *125*, 16194.
- X. Ma, H. Wang, W. Chen, *J. Org. Chem.* **2014**, *79*, 8652.
- Y. Kim, Y. Kim, M. Y. Hur, E. Lee, *J. Organomet. Chem.* **2016**, *820*, 1.
- N. Marion, O. Navarro, J. Mei, E. D. Stevens, N. M. Scott, S. P. Nolan, *J. Am. Chem. Soc.* **2006**, *128*, 4101.
- M. S. Viciu, R. M. Kissling, E. D. Stevens, S. P. Nolan, *Org. Lett.* **2002**, *4*, 2229.
- L. C. Campeau, P. Thansandote, K. Fagnou, *Org. Lett.* **2005**, *7*, 1857.
- N. M. Scott, R. Dorta, E. D. Stevens, A. Correa, L. Cavallo, S. P. Nolan, *J. Am. Chem. Soc.* **2005**, *127*, 3516.
- U. Christmann, R. Vilar, *Angew. Chem. Int. Ed. Engl.* **2005**, *44*, 366.
- E. S. Chernyshova, R. Goddard, K.-R. Pörschke, *Organometallics* **2007**, *26*, 3236.
- E. Lee, D. V. Yandulov, *J. Organomet. Chem.* **2011**, *696*, 4095.
- E. Lee, D. Y. Bae, S. Park, A. G. Oliver, Y. Kim, D. V. Yandulov, *Eur. J. Inorg. Chem.* **2016**. doi:10.1002/ejic.201601019.
- W. A. Herrmann, V. P. W. Böhm, C. W. K. Gstöttmayr, M. Grosche, C.-P. Reisinger, T. Weskamp, *J. Organomet. Chem.* **2001**, *617–618*, 616.
- A. Flahaut, K. Toutah, P. Mangeney, S. Roland, *Eur. J. Inorg. Chem.* **2009**, *2009*, 5422.
- M. J. Frisch, et al., Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford, CT, **2010**.