

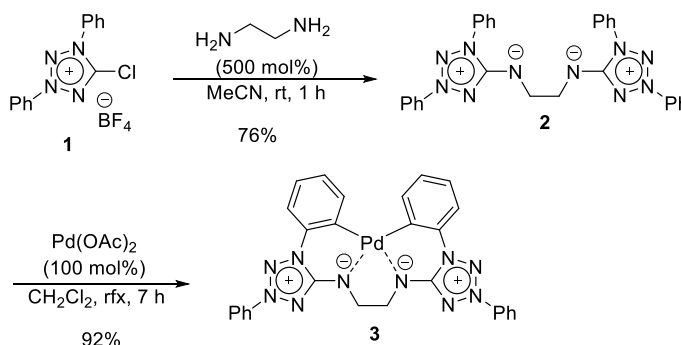
Synthesis of palladium complexes with mesoionic tetrazolium-5-aminides

(Graduate School of Engineering, Nagoya Institute of Technology) ○ KURABAYASHI Hideaki, HIRASHITA Tsunehisa

Keywords: Mesoionic compounds, Nitrogen ligands, Pd complexes

Mesoionic compounds are heterocyclic compounds in which both the negative and the positive charge are delocalized. The formal positive charge is associated with the ring atoms, and the formal negative charge is associated with ring atoms or an exocyclic nitrogen or chalcogen atom. The negatively charged exocyclic atom is expected to coordinate to a metal center as a strong ligand, while only a few complexes with mesoionic compounds have been reported.¹ In this study, we have synthesized mesoionic tetrazolium-5-amide compounds and their complexes with palladium (II) salts.

5-Chloro-1,3-diphenyltetrazolium tetrafluoroborate (**1**) was reacted with ethylenediamine (500 mol%) in acetonitrile for 1 h at room temperature to give the mesoionic diamide **2** in 76% yield. The reaction of **2** with Pd(OAc)₂ (100 mol%) in CH₂Cl₂ under reflux conditions for 7 h gave the palladacycle **3** in 92% yield (Scheme 1). Single crystal X-ray structure analysis of **3** (Figure 1) revealed that the distances of the Pd-N bonds are relatively short (2.055 Å), compared with those of other amine complexes (2.06–2.20 Å).



Scheme 1. Synthesis of a mesoionic nitrogen ligand **2** and a palladacycle **3**.

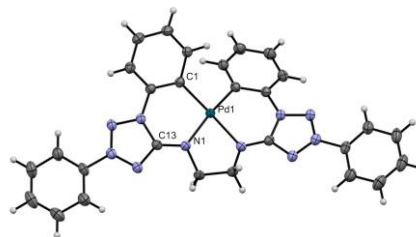


Figure 1. X-ray crystal structure of **3**. Solvent molecules omitted for clarity; ellipsoids drawn at 50% probability. Select bond lengths (Å) : Pd1-N1 2.055, Pd1-C1 2.009, N1-C13 1.304.

- 1) a) Araki, S.; Butsugan, Y. *Chem. Ber.* **1993**, *126*, 1157-1158. b) Vaddypally, S.; Tomlinson, W.; O'Sullivan, T. O.; Ding, R.; Van Vliet, M. M.; Wayland, B. B.; Hooper, P. J.; Zdilla, J. M. *J. Am. Chem. Soc.* **2019**, *141*, 5699-5709. c) Vaidya, S.; Upadhyay, A.; Singh, K. S.; Gupta, T.; Tewary, S.; Langley, K. S.; Walsh, P. S. J.; Murray, S. K.; Rajaraman, G.; Shanmugam, M. *Chem. Commun.*, **2015**, *51*, 3739-3742. d) Zhao, Y.; Li, L.; Yan, R.; Wu, F.; Zhang, J.; Guo, Z.; Wu, Y. *J. Mol. Struct.* **2018**, *1156*, 30-33.