

DIAZO

The logo for DIAZO 2021 features the word "DIAZO" in a bold, black, sans-serif font. Below it, the year "2021" is written in a large, blue, sans-serif font. To the left of "2021" is a black square containing a blue "N₂" symbol, representing a diazo group.

**VI International Symposium
«The Chemistry of Diazo Compounds
and Related Systems»**

Saint Petersburg, Russia, September 6-10

**BOOK OF
ABSTRACTS**

Pd^{II} AND Pt^{II}-MEDIATED COUPLING OF ARYL ISOCYANIDES WITH N-HETEROCYCLIC THIONES AS A WAY TO MONO- AND POLYNUCLEAR AMINOCARBENE COMPLEXES

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In recent decades, transition metal complexes with aminocarbene ligands (NHC – N-heterocyclic carbenes, ADC – acyclic diaminocarbenes) have taken a special place in coordination and organometallic chemistry due to their wide application in catalysis, material design, and medical chemistry [1]. One of the promising and facile methods for generating complexes with various types of aminocarbene ligands is the metal-mediated addition of nucleophiles to coordinated isocyanides [2].

In the present work, we have studied the Pd^{II} and Pt^{II}-mediated coupling of aryl isocyanides with N-heterocyclic thiones acting as ambident S,N-nucleophiles. The reaction of equimolar amounts of bis(aryl isocyanide) complexes and corresponding thione in the presence of one equivalent of base leads to the formation of mononuclear C,S-chelated aminocarbene complexes in which the carbene fragment is formed by the endocyclic nitrogen atom of thione and the triple CN of an isocyanide ligand (Figure 1) [3]. At the same time, the utilization of an excess of a base in the reaction with unsubstituted thiones yields the deprotonation of the formed complexes and allows obtaining polynuclear coordination macrocyclic compounds, which structure was confirmed both in a solution (by NOESY and DOSY NMR technics, mass-spectrometry) and in a solid state (by single-crystal X-ray diffraction). However, the latter compounds could be downgraded again to the mononuclear species by the addition of triphenylphosphine (PPh₃).

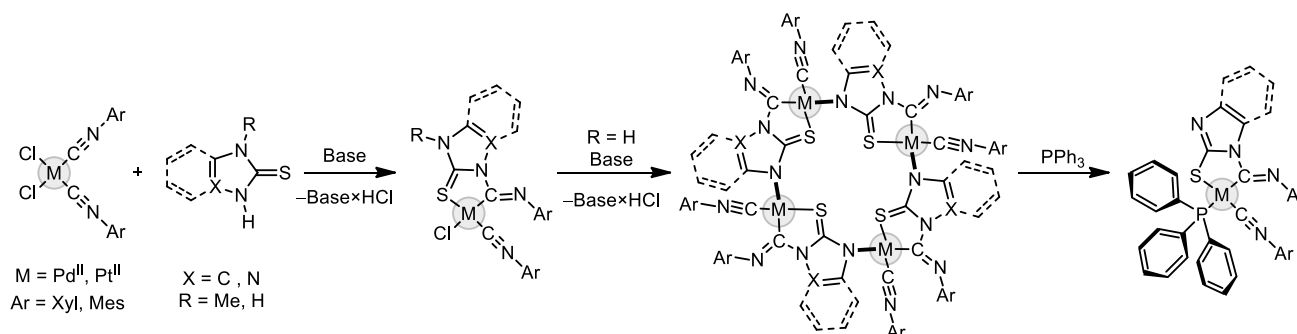


Figure 1. Coupling of bis-(aryl isocyanide) Pd^{II} and Pt^{II} complex with N-heterocyclic thiones.

References

- [1] Hopkinson M. N. *et al. Nature.* **2014**, *510*, 485–496
- [2] Boyarskiy V. P. *et al. Chemical reviews.* **2015**, *115*, 2698–2779
- [3] Popov R. A. *et al. New Journal of Chemistry.* **2021**, *45*, 1785–1789.

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