

INFLUENCE OF P/N DONOR SET COMPOSITION IN PHOSPHINE/OXAZOLINE LIGANDS ON ELECTROCHEMICAL STABILITY OF LOW-VALENT NICKEL AND COBALT COMPLEXES

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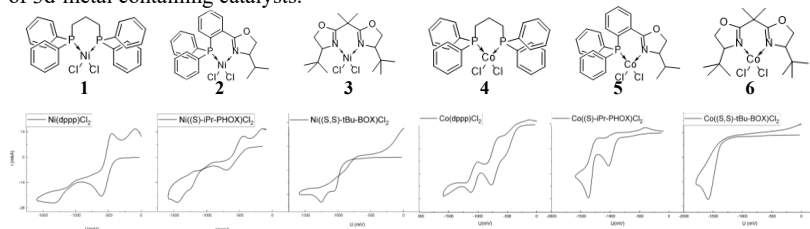
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Phosphine complexes of cobalt and nickel have been widely studied in recent decades as catalysts for various organic transformations such as cross-couplings, intermolecular cyclizations and metallation of aromatic halides. Such compounds have good potential of application instead of precious metal complexes. Previously, we have found that electrochemical stability of low-valent metal complexes was crucial for high catalytic activity in reactions involving oxidative addition of aryl halides [1]. However, phosphine ligands of complex structure, especially chiral, are quite expensive, and search of alternative ligand systems, which efficiently stabilize low-valent Ni and Co, is an actual task.

The aim of the work was to determine the effect of phosphine substitution by oxazoline residues on the electrochemical stability of Ni and Co complexes in low oxidation states. Oxazoline fragments were chosen due to simple formation of chiral centers, which is important for asymmetric catalytic reactions. Six cobalt and nickel complexes were synthesized and their redox properties were investigated by cyclic voltammetry. It was found that Ni(dppp)Cl<sub>2</sub> (**1**) was the only one, which possessed completely reversible redox process Ni<sup>II</sup>/Ni<sup>I</sup>, while Ni((S)-iPr-PHOX)Cl<sub>2</sub> (**2**) was reduced irreversibly to Ni<sup>I</sup> and Ni<sup>0</sup>. Reduced forms of Co(dppp)Cl<sub>2</sub> (**4**) and Co((S)-iPr-PHOX)Cl<sub>2</sub> (**5**) could be partially reoxidized, however, Co((S,S)-tBu-BOX)Cl<sub>2</sub> (**6**) and also Ni((S,S)-tBu-BOX)Cl<sub>2</sub> (**3**) underwent complete decomposition upon reduction to M<sup>I</sup> under experimental conditions. Notably, the potentials of Ni complexes reduction were more positive compared to their Co congeners.

In general, introduction of just one phosphorus atom into M(P/N)<sub>2</sub>Cl<sub>2</sub> chromofors drastically improved stability of M<sup>I</sup> complexes both on criteria of redox potential and CV process reversibility. These findings can be used for further improvement of the ligand design of 3d-metal containing catalysts.



## References

1. M. O. Ivanytsya, O. O. Pariiska, A. M. Mishura, E. B. Rusanov, S. V. Shishkina, A. O. Gorlova, A. S. Lytvynenko, S. V. Ryabukhin, D. M. Volochnyuk, S. V. Kolotilov. *Inorg. Chem.* **2023**, 62, 15, 5906–5919.