NEW CONTROLLED REACTIVITY IN COORDINATED ISOCYANIDES: INSERTION REACTIONS AND CREATION OF NEW C-C AND C-N BONDS

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It is well-known that nickel (II) can promote isocyanide polymerization, and Ni(II) complexes have been used as catalysts in the industrial process for decades. On the other hand, the reactivity of coordinated isocyanides with amines to obtain metallic carbenes has been widely studied. Now, another reactivity has been explored and isocyanide insertion reactions have been found to take place in the coordination sphere of Ni(II) complexes by the addition of different nucleophiles. The initial nucleophilic attack promotes C-C and C-N coupling processes that are followed by five-member ring-closure reactions. In this way, cationic and neutral complexes of 2, 3 or even 4 isocyanides can be coupled (*Figure 1*), and their structure has been unequivocally characterized by X-ray diffraction as well as various spectroscopy techniques (IR, NMR…) [1,2]. A mechanism for this transformation is proposed on the basis of additional NMR studies. Mixed-isocyanide species have been obtained, which confirm this proposal. The number of insertions, and consequently the number new C-C and C-N bonds created, can be controlled depending on the nucleophile.

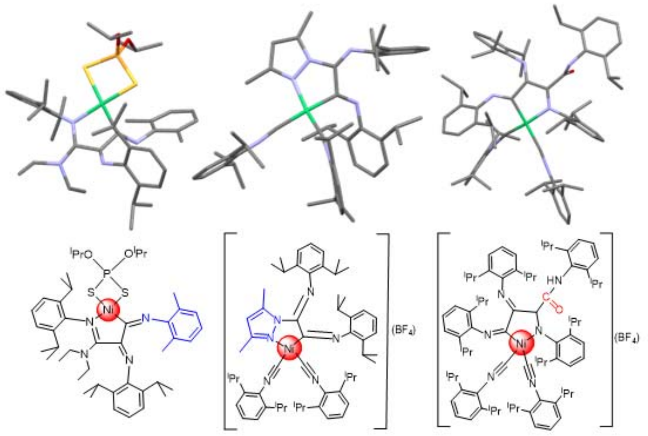

Figure 1. Neutral and cationic inserted isocyanide complexes of Ni(II).

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[1] O. Romano V. A. et al., *Angew.Chem. Int.Ed.,* **2020**, *59*, 540 –558.

[2] L. Ming et al. *Org. Lett.*, **2018**, *20*, 7158−7162.