

## Metal-NHC Dynamics in Organometallic Chemistry and Catalysis

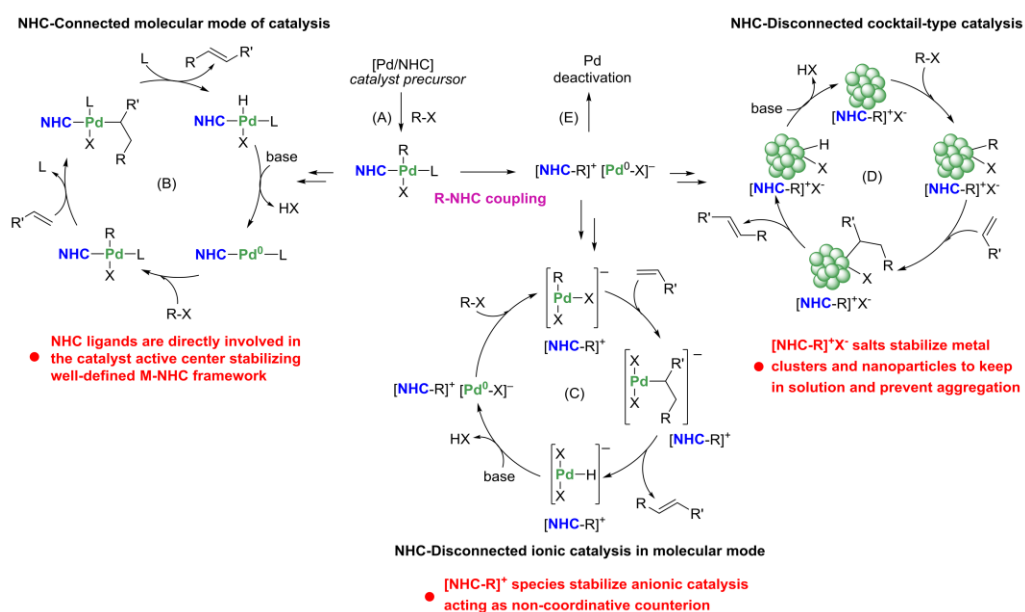
Valentine P. Ananikov

Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences

Leninsky Prospekt 47, Moscow, Russia; <http://AnanikovLab.ru>

N-heterocyclic carbenes (NHCs) are superior ligands for binding with transition metals and forming unique structures. High stability on air, stable metal-ligand framework and outstanding possibility to tune electronic and steric properties (by varying types of NHC rings and substituents) has led to a large variety of metal complexes with numerous applications in chemistry and catalysis. Applications of Metal/NHC (M/NHC) complexes in homogeneous catalysis are of particular importance, where a paramount progress was demonstrated in recent decades [1].

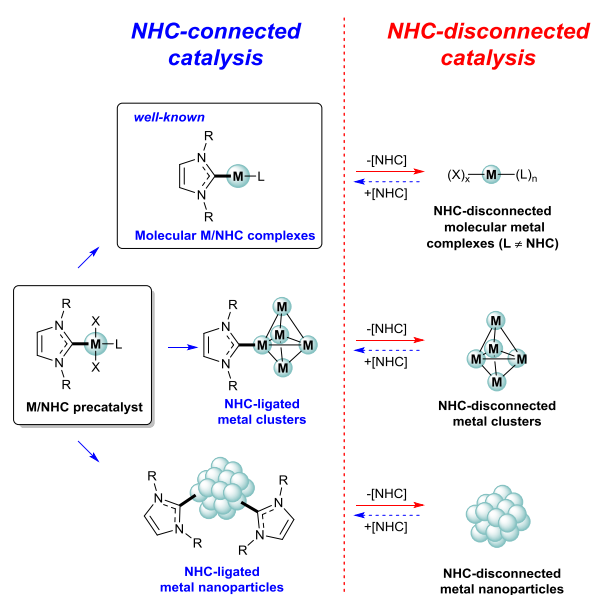
Detailed mechanistic studies have revealed a unique picture with dual opportunities in catalysis: i) homogeneous catalysis with molecular M/NHC complexes, and ii) nanoparticle catalysis with NHC-stabilized metal clusters. The interchange between two types of catalysis was first described upon studying a well-known Mizoroki-Heck reaction [2]. A new mode of catalysis, which takes an advantage of chemical lability of the M-NHC bond (rather than stability, as it was previously assumed), was revealed in the experiment [2]. Facile R-NHC coupling was shown to be a general process for various metal complexes and organic groups R [3,4,5,6], thus opening excellent possibilities for in situ generation of stabilized metal clusters and nanoparticles from M/NHC precursors. A possibility of the reverse process (R-NHC oxidative addition) and NHC-mediated leaching of metal species from the surface of nanoparticles [7] give rise to construction of dynamic catalytic systems.



**Figure 1.** Universal range of catalytic systems accessible from M/NHC complexes (image from ref. [8], (C) The Royal Society of Chemistry, CC-BY-NC license).

Detailed analysis of the literature has shown that M-NHC dynamics indeed may be present in a number of systems for various metals and NHC ligands [8]. Using a single M/NHC complex three types of catalytic systems may be generated: i) molecular catalysis, ii) nanoparticle catalysis, and iii) ionic catalysis (Figure 1) [8]. It appears that many M/NHC-catalyzed reactions may involve dynamic and cocktail-type systems with dynamic interconversion of active species during the reaction.

Interestingly, NHC ligands continue to play an important role in the stabilization of metal centers after breakage of the M-NHC bond. Stabilization of metal clusters and nanoparticles via azolium species or stabilization of molecular ionic complexes via counterion interactions were discussed (Figure 1) [8].



**Figure 2.** Single M/NHC complex as a universal precursor for a number of tuned catalytic systems (image from ref. [8], (C) The Royal Society of Chemistry, CC-BY-NC license).

Intrinsic dynamic behavior recalls for more studies on the synthesis, structure, stability and reactivity of M/NHC complexes in organometallic chemistry. New wave of dynamic and cocktail-type catalysts design based on the M/NHC complexes is anticipated in the near future for development of a new generation of catalytic systems. Formulation of the concept of “NHC-connected” and “NHC-disconnected” modes of catalysis (Figure 2) [8] is of much importance to develop efficient and recyclable catalytic systems. Thus, understanding the role of NHC ligands and controlling the nature of catalytic centers becomes the topic of key importance.

## References

- [1] (a) E. Peris. Smart N-Heterocyclic Carbene Ligands in Catalysis. *Chem. Rev.* 2018, **118**, 9988-10031. [DOI]
- (b) S. Budagumpi, R. S. Keri, G. Achar, and K. N. Brinda. Coinage Metal Complexes of Chiral N-Heterocyclic Carbene Ligands: Syntheses and Applications in Asymmetric Catalysis. *Adv. Synth. Catal.* 2020, **362**, 970-997. [DOI]
- (c) W.A. Herrmann. N-Heterocyclic Carbenes: A New Concept in Organometallic Catalysis. *Angew. Chem. Int. Ed.* 2002, **41**, 1290-1309. [DOI]

- 
- (d) E. Kantchev, C. O'Brien, and M. Organ. Palladium Complexes of N-Heterocyclic Carbenes as Catalysts for Cross-Coupling Reactions—A Synthetic Chemist's Perspective. *Angew. Chem. Int. Ed.* 2007, **46**, 2768-2813. [\[DOI\]](#)
- (e) C. Fliedel, A. Labande, E. Manoury, and R. Poli. Chiral N-heterocyclic carbene ligands with additional chelating group(s) applied to homogeneous metal-mediated asymmetric catalysis. *Coord. Chem. Rev.* 2019, **394**, 65-103. [\[DOI\]](#)
- (f) R.D.J. Froese, C. Lombardi, M. Pompeo, R.P. Rucker, and M. Organ. Designing Pd–N-Heterocyclic Carbene Complexes for High Reactivity and Selectivity for Cross-Coupling Applications. *Acc. Chem. Res.* 2017, **50**, 2244–2253. [\[DOI\]](#)
- (g) T. Simler, and P. Braunstein. N-Heterocyclic Carbene Complexes of Copper, Nickel, and Cobalt. *Chem. Rev.* 2019, **119**, 3730–3961. [\[DOI\]](#)
- (h) D. Janssen-Müller, C. Schleppehorst, and F. Glorius. Privileged chiral N-heterocyclic carbene ligands for asymmetric transition-metal catalysis. *Chem. Soc. Rev.* 2017, **46**, 4845-4854. [\[DOI\]](#)
- (i) G.C. Fortman, and S.P. Nolan. N-Heterocyclic carbene (NHC) ligands and palladium in homogeneous cross-coupling catalysis: a perfect union. *Chem. Soc. Rev.* 2011, **40**, 5151-5169. [\[DOI\]](#)
- (j) V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt, and S. Inoue. NHCs in Main Group Chemistry. *Chem. Rev.* 2018, **118**, 9678–9842. [\[DOI\]](#)
- (k) T. Dröge, and F. Glorius. The Measure of All Rings—N-Heterocyclic Carbenes. *Angew. Chem. Int. Ed.* 2010, **49**, 6940-6952. [\[DOI\]](#)
- [2] A.V. Astakhov, O.V. Khazipov, A.Yu. Chernenko, D.V. Pasyukov, A.S. Kashin, E.G. Gordeev, V.N. Khrustalev, V.M. Chernyshev, and V.P. Ananikov. A New Mode of Operation of Pd-NHC Systems Studied in a Catalytic Mizoroki–Heck Reaction. *Organometallics* 2017, **36**, 1981-1992. [\[DOI\]](#)
- [3] E.G. Gordeev, D.B. Eremin, V.M. Chernyshev, and V.P. Ananikov. Influence of R–NHC Coupling on the Outcome of R–X Oxidative Addition to Pd/NHC Complexes (R = Me, Ph, Vinyl, Ethynyl). *Organometallics* 2018, **37**, 787-796. [\[DOI\]](#)
- [4] O.V. Khazipov, M.A. Shevchenko, A.Yu. Chernenko, A.V. Astakhov, D.V. Pasyukov, D.B. Eremin, Y.V. Zubavichus, V.N. Khrustalev, V.M. Chernyshev, and V.P. Ananikov. Fast and Slow Release of Catalytically Active Species in Metal/NHC Systems Induced by Aliphatic Amines. *Organometallics* 2018, **37**, 1483-1492. [\[DOI\]](#)
- [5] A.V. Astakhov, S. Soliev, E.G. Gordeev, V.M. Chernyshev and V. P. Ananikov. Relative Stability of M/NHC Complexes (M = Ni, Pd, Pt) against R–NHC, X–NHC and X–X Couplings in M(0)/M(II) and M(II)/M(IV) Catalytic Cycles: a Theoretical Study. *Dalton Trans.*, 2019, **48**, 17052-17062. [\[DOI\]](#)
- [6] D.B. Eremin, E.A. Denisova, A.Yu. Kostyukovich, J. Martens, G. Berden, J. Oomens, V.N. Khrustalev, V. M. Chernyshev, and V. P. Ananikov, *Chem. – Eur. J.* 2019, **25**, 16564. [\[DOI\]](#)
- [7] E.A. Denisova, D.B. Eremin, E.G. Gordeev, A.M. Tsedilin, and V.P. Ananikov. Addressing Reversibility of R–NHC Coupling on Palladium: Is Nano-to-Molecular Transition Possible for the Pd/NHC System? *Inorg. Chem.* 2019, **58**, 12218-12227. [\[DOI\]](#)
- [8] V.M. Chernyshev, E.A. Denisova, D.B. Eremin, and V.P. Ananikov. The key role of R–NHC coupling (R = C, H, heteroatom) and M–NHC bond cleavage in the evolution of M/NHC complexes and formation of catalytically active species. *Chem. Sci.*, 2020, **11**, 6957-6977. [\[DOI\]](#)