



Review

Catalysis by 1,2,3-triazole- and related transition-metal complexes

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ABSTRACT

A short overview of the multiple coordination modes of 1,2,3-triazole- and related transition-metal complexes are provided, then the implication of and catalysis with transition-metal-1,2,3-triazole complexes are detailed with Mn, Fe, Ni, Cu, Ru, Rh, Ir, Pd, and Au catalysts including various ligand coordination modes and mechanistic features.

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1. Introduction

The 1,2,3-triazole heterocycle, known since the end of the 19th century, is now a common heterocyclic ligand in chemistry and biology [1]. Relatively few studies have been reported before the year 2000 due to the limited availability of functional triazole derivatives when the non-selective Huisgens reaction was used for their synthesis [1b,1c]. The breakthrough in triazole chemistry came in the early 2000s with a novel concept, that of “click” chemistry, that was first fully presented by Sharpless’ group [2,3]. The “click” reactions described chemistry tailored to quickly and reliably generate substances by linking small units together under “green” conditions. This has proved to be a powerful concept allowing molecule fragments to assemble. Indeed, the most popular reaction representing the “click” chemistry concept is the Cu-catalyzed alkyne–azide (CuAAC) reaction with the regioselective formation of 1,4-disubstituted 1,2,3-triazoles [4]. Besides, the Ru-catalyzed alkyne–azide (RuAAC) reaction was later disclosed to also regioselectively form 1,2,3-triazoles, but at this time with 1,5-disubstitution [5]. Thanks to these modular, facile and high-yield methods for the generation of a large number of 1,2,3-triazoles and their derivatives, 1,2,3-triazole heterocyclic chemistry now appears as a new area with potential applications of 1,2,3-triazole-metal complexes in optics, redox sensing, biomedicine and catalysis [6]. Transition-metal triazole and triazolyl complexes have recently present catalytic activity for a number of organic reactions, and the purpose of this review is to survey these properties and catalytic reactions.

2. Coordination modes of triazole and triazolyl ligands with transition metals

1,2,3-Triazoles bearing several donor sites are potentially versatile ligands for metal coordination [7]. Generally, there are mainly three modes with which triazole ligands combine with transition metals (Figs. 1, 3 and 4). The first mode is through nitrogen coordination of neutral simple triazoles and chelating triazoles (Fig. 1). DFT calculations have shown that *N3* is a better donor compared to *N2* [8]. The triazole ligand coordinates to a metal through the *N3* nitrogen atom either as a monodentate ligand (type A) or as part of a bi- or poly-dentate chelator (type B), when there are other

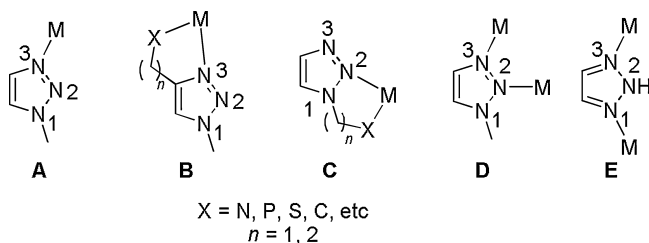


Fig. 1. Simple triazoles and chelating triazoles coordinate to transition metals.

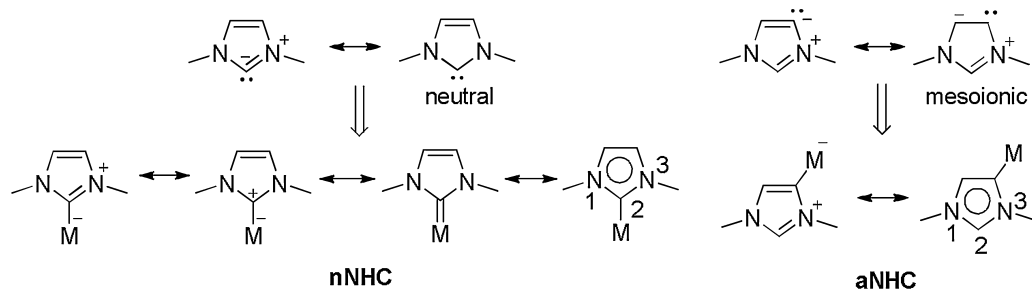


Fig. 2. Imidazole-based nNHCs and aNHCs.

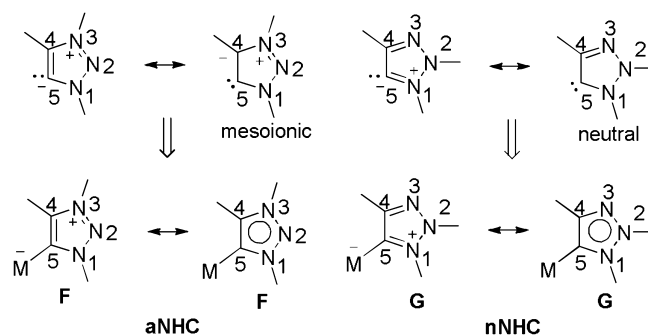


Fig. 3. Deprotonated triazolium ligands (NHCs) transition metal complexes.

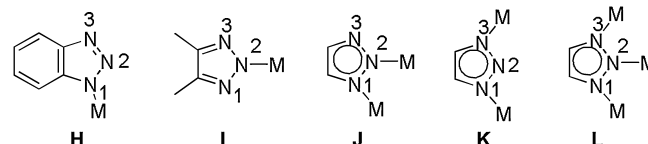


Fig. 4. Deprotonated NH 4,5-disubstituted triazolates as anionic ligands in transition metal complexes.

donor sites nearby. When the additional donor site is adjacent to *N1*, coordination through *N2* is possible to form a bi- or poly-dentate chelator (type C) [9]. Thus, for the metal chelators, five- or six-membered cycles are usually formed. Besides, bridging coordination modes with two metals coordinating to two of the nitrogen atoms are possible (types D and E).

The second mode is C5 coordination with deprotonated triazoliums to form *N*-heterocyclic carbenes (NHCs, Fig. 3). NHCs are a class of well-known, very useful ligands resulting from the deprotonation of imidazolium salts, but members of the family are also obtained by deprotonation of triazolium salts. NHCs are stronger neutral electron donors (σ donors), have a better oxidation stability and undergo easier modification than tertiary phosphines. Therefore, they have been widely used as ligands with success in transition metal catalysis [10]. Imidazolium salts are the most frequently used carbene precursors with metal bounded at the C2 position. Subsequently, imidazole-based carbenes with the metal bonded at the C4(5) position were also first reported by Crabtree and co-workers (Fig. 2) [11]. These carbenes are called “abnormal” *N*-heterocyclic carbenes (aNHCs), and they are even stronger σ donors than C2-bound “normal” *N*-heterocyclic carbenes (nNHCs) [12]. The difference between these two classes of carbenes is that free nNHCs have a resonance form with all-neutral formal charges, while the free aNHC are mesoionic (Fig. 2). In 2008, Albrecht and co-workers used 1,3,4-substituted 1,2,3-triazolium salts as precursors for the synthesis of new aNHCs with various transition metals [13]. These abnormal triazolylidene complexes (type F) are expected to have a great potential for the development of new catalysts with unprecedented reactivities. Recently, an example

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