



Digest paper

Silver-catalyzed organic reactions of isocyanides

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ABSTRACT

The combined chemistry of silver and isocyanides is unique in performance, proved with the number of recent achievements. With the aim of triggering further research in this field, this review assembles and comprehensively summarizes the silver-based reactions of isocyanides. In this review, we especially emphasize the uniqueness of silver catalysis in the activation of isocyanides, the reaction selectivity, and the mechanistic description.

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Introduction

Transition metal (TM) catalyzed organic synthesis has become useful in academics and industries in the past decade.¹ This is because TM-catalysis allows the use of simple starting materials to synthesize complex organic molecules. Silver catalysts are not only more economical than other frequently used transition metal catalysts, but more importantly, they are environmentally benign.

Hence silver catalysis is a very attractive option for organic synthesis, and its use in industry is rising at an incredible rate.² The rapid deployment of silver chemistry could be verified from the large number of reviews published in the last ten years³ including ours.⁴ The silver salts perform the Lewis acid character owing to the availability of empty *f*-orbitals and relativistic contraction of the electron cloud. Interestingly, silver salts are able to act as either σ -Lewis acid or π -Lewis acid, with preference of σ -coordination over π -coordination. Silver salts could coordinate to the unsaturated systems like C=C, C≡C, C=X, and C≡X bonds (X is hetero atom). According to our short survey, silver salts were utilized in organic synthesis not only as Lewis acids, but also as co-catalysts, halophiles, general oxidants, SET oxidants (SET = single electron transfer), weak bases, and radical precursors. Because of all these

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advantages, silver catalysis has provided new avenues in the field of organic synthesis.^{2–4}

On the other hand, isocyanides (isonitriles/carbylamines) are a class of fundamental chemicals. Since the discovery of the Passerini and Ugi reactions, isocyanides were well-known as reagents for multi-component reactions.⁵ In the past decades, isocyanides have proved to be highly useful reagents in organic synthesis, because they could play various roles as electrophiles, nucleophiles, carbenes, carbon monoxide equivalents, 1,3-dipoles, and multi-functional reagents, etc.^{6,7} Apparently, isocyanide chemistry is one of the broad and important fields of organic chemistry.

The ability of silver salts to coordinate to unsaturated bonds led the silver catalysis to activate isocyanide ($-\text{N}\equiv\text{C}$) functionality. Numerous achievements were reported, including our contribution towards the development of silver-catalyzed chemistry of isocyanides.⁸ Until now, a book⁶ and several reviews⁷ exploring the chemistry of isocyanides has been published. To the best of our knowledge, however, a review emphasizing the significance and the achievements of the silver-based isocyanide chemistry has not been published.

In the view of the unique nature of silver catalysis in isocyanide chemistry, a special review would be timely for further promoting this field. We therefore would like to deliver such a survey on the developments in the silver-catalyzed reactions of isocyanides. This review provides a comprehensive view of all the achievements to date in the silver-catalyzed isocyanide chemistry. These will be arranged in the sequence of reactions with double bonds, alkynes, radicals, and isocyanides as dipolarophile, and miscellaneous reactions. Notably, the examples involving silver(I) salts as the part of co-catalysis will not be illustrated.

Reactions with double bonds

Double bonds are ubiquitous in organic molecules. Isocyanides substituted with electron-withdrawing groups like carboxylic esters, nitriles, phosphonic esters, or sulfonyl groups at α -position could act as 1,3-dipoles in the reactions with versatile double bond systems. Not surprisingly, many studies based on the transition metals catalytic systems have been developed (Fig. 1).

Asymmetric aldol-type condensation of isocyanides with aldehydes or ketones was extensively investigated under the catalysis of a number of transition metal complexes. The dominant *trans*-oxazolines formation was observed with Au(I),⁹ Cu(I),^{9f,10} Ag(I), Pt(II),¹¹ Pd(II),^{9f,11a–d,12} Pt(IV),^{12d} Co(II),¹³ Ru(II),¹⁴ Rh(I)^{9f} catalysts, etc. Enantioselective reactions have also been comprehensively investigated. Oxazoline formation with high *ee* values were afforded by using asymmetric Au(I), Ag(I), Co(II) catalysts, however, the enantioselectivities were decreased to

modest, even low grade in the present of Pt and Pd pincer complexes.

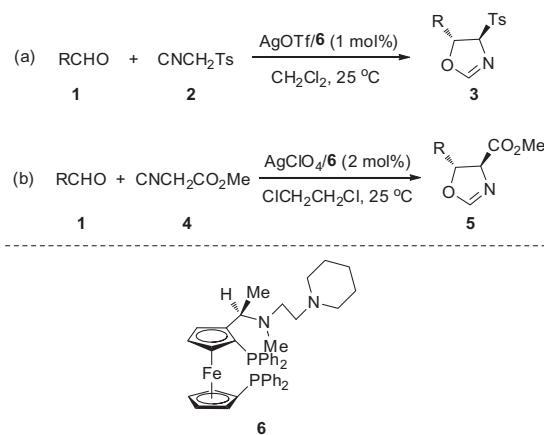
Although imines performed somewhat low reactivity, many reports on the asymmetric Mannich-type reaction of isocyanides with imines were still available. Transition metals, such as Au(I),¹⁵ Pd(II),^{15a,16} Cu(I),^{15a} Rh(II),^{15a,17} Cu(II),¹⁸ Ag(I)¹⁹ and Ru(II),^{15a,20} were successfully utilized in the synthesis of imidazolines. Interestingly, the *cis*-products with high diastereoselectivity were obtained by using Au(I) catalyst.¹⁵

Besides the reaction with polarized double bonds (carbonyl or imine groups), alkenes were used as reaction partners catalyzed by Cu,²¹ Au,²² and Ag,²³ as well. In the following section, only silver-catalyzed reactions of isocyanides with double bonds are discussed in detail.

Synthesis of chiral aza-heterocycles

In 1990, the Ito group reported the synthesis of optically active 5-alkyl-4-tosyl-2-oxazolines **3** with high *ee* values by reaction of aldehydes **1** with tosylmethyl isocyanide (TosMIC) **2** (Scheme 1, a).²⁴ This reaction was catalyzed by chiral Ag(I) complex made from AgOTf and ferrocene ligand **6**. This Ag(I) catalyst was effective to a variety of aromatic aldehydes, aliphatic aldehydes and α,β -unsaturated aldehydes. Later in 1991, Hayashi et al. extended this reaction to methyl isocyanoacetate **4** (Scheme 1, b).²⁵

In 1994, the Hayashi group reported silver/NEt₃-catalyzed highly *cis*-diastereoselective [3 + 2]cycloaddition reaction of aryl fluoroalkyl ketones **7** with methyl isocyanoacetate **4** (Scheme 2).²⁶ Notably, the high *cis*-diastereoselectivity was limited to only



Scheme 1. [3 + 2]Cycloaddition reaction of isocyanides with aldehydes.

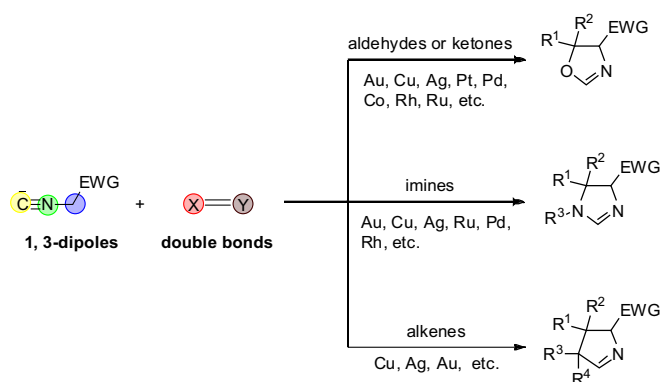
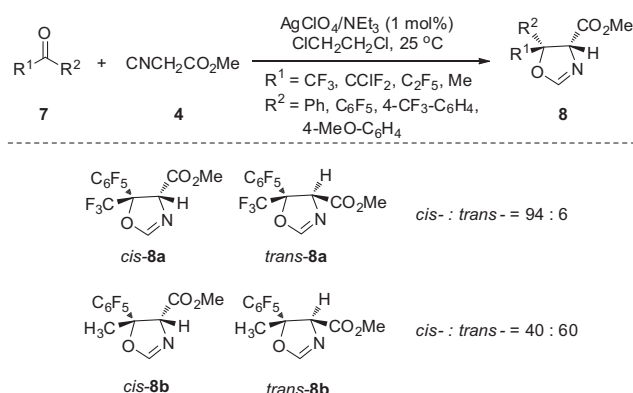


Fig. 1. TM-catalyzed reaction of isocyanides with double bonds.



Scheme 2. Reaction of methyl isocyanoacetate with ketones.

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