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Transition metal-catalyzed addition of C-, N- and O-nucleophiles to unactivated C–C multiple bonds

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Abbreviations: acac, acetylacetonate; aq, aqueous; Ac–, acetyl; Ar, aryl; atm, atmosphere; BMIM, 1-butyl-3-methylimidazolium; Bim, bis(1-methylimidazol-2-yl)methane; BHT, butylated hydroxytoluene; BINAP, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl; Bpm, bis(1-pyrazolyl)methane; Bn, benzyl; Bz, benzoyl; ^{n}Bu, *n*-butyl; ^{t}Bu, *tert*-butyl; Boc, *tert*-butoxycarbonyl; cat., catalyst; Cbz, benzyloxycarbonyl; cod, 1,5-cyclooctadiene; cot, 1,3,5-cyclooctatriene; Cp, cyclopentadienyl; Cp*, pentamethylcyclopentadienyl; Cbz, benzyloxycarbonyl; Cy, cyclohexyl; (Cy)$_2$ATI, *N*-cyclohexyl-2-(cyclohexylamino)troponiminate; dba, dibenzylideneacetone; DABCO, 1,4-diazabicyclo[2.2.2]octane; DCM, dichloromethane; DMAP, 4-dimethylaminopyridine; dpph, 6-(3,5-dimethyl-1*H*-pyrazol-1-yl)picolinic acid; dppb, 1,4-bis(diphenylphosphino)butane; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; DMF, *N*,*N*-dimethylformamide; d-i-prpf, 1,1′-bis(diisopropylphosphino)ferrocene; DPPE, 1,2-bis(diphenylphosphino)ethane; dppf, 1,1′-bis(diphenylphosphino)ferrocene; dipea, *N*,*N*-diisopropylethylamine; DPPP, 1,3-bis(diphenylphosphino)propane; dppm, bis(diphenylphosphino)methane; DCypp, 1,3-bis(dicyclohexylphosphino)propane; Dipp, 2,6-diisopropylphenyl; DPPB, 1,4-bis(diphenylphosphino)butane; DCE, 1,2-dichloroethane; DMA, *N*,*N*-dimethylacetamide; DMAD, dimethyl acetylenedicarboxylate; DME, 1,2-dimethoxyethane; equiv, equivalent; Et, ethyl; Fmoc, fluorenylmethyloxycarbonyl; ^{n}Hex, *n*-hexyl; ^{n}Hept, heptyl; Ind, indenyl; IMes, 1,3-dimesitylimidazol-2-ylidene; KHMDS, potassium bis(trimethylsilyl)amide; Ms, methanesulfonyl; MOM, methoxymethyl; M, metal; Me, methyl; min, minutes; MW, microwave; Mes, 2,4,6-trimethylphenyl; NHC, *N*-heterocyclic carbene; NHS, *N*-hydroxysuccinimide; NP, nanoparticle; naphth, naphthyl; ^{n}Oct, *n*-octyl; ^{n}Pent, *n*-pentyl; Py, pyridine; PPTS, pyridinium *p*-toluenesulfonate; Ph, phenyl; ^{i}Pr, *iso*-propyl; PTA, 1,3,5-triaza-7-phosphaadamantane; PVP, polyvinylpyrrolidone; PMP, *p*-Methoxyphenyl; Piv, pivaloyl; PAMAM, poly(amidoamine); rt, room temperature; s, seconds; TBAB, tetrabutylammonium bromide; TFA, trifluoroacetic acid; TDMPP, tris(2,6-dimethoxyphenyl)phosphine; TMU, tetramethylurea; Tp, trispyrazolylborate; Tf, triflyl; Ts, *p*-toluenesulfonyl; TPPTS, tris(3-sulfophenyl)phosphine trisodium salt; TBDMS, *tert*-butyldimethylsilyl; TBDPS, *tert*-butyldiphenylsilyl; Tf, trifluoromethanesulfonyl; THF, tetrahydrofuran; TBAF, tetrabutylammonium fluoride; TMS, trimethylsilyl; TEMDA, *N*,*N*,*N*′,*N*′-tetramethyl-ethane-1,2-diamine; TIPS, triisopropylsilyl; Troc, 2,2,2-trichlorethoxycarbonyl; TOF, turnover frequency; TON, turnover number; Triphos, bis(2-diphenylphosphinoethyl)phenylphosphine; Xantphos, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene.

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1. Introduction

The additions of various nucleophiles (X—H) to carbon—carbon (C—C) multiple bonds are of prime importance in synthetic organic chemistry. These essentially simple reactions allow the formation of XC—CH bonds in an atom-efficient manner. The Michael reaction, the addition of a nucleophile onto a C—C multiple bond bearing electron-withdrawing group/s, is one of the oldest reactions known for the formation of C—C and C—X bonds. This reaction of fundamental simplicity represents the most atom-economical process for the synthesis of important bulk and fine chemicals or building blocks in organic synthesis. However, the reaction is applicable only for activated C—C multiple bonds and nucleophiles (X—H) generally do not add to C—C multiple bonds as long as they are not activated by electron-withdrawing substituents (Michael reactions). This lack of reactivity is obviously due to electrostatic reasons, since both the species are electron-rich. Therefore, the use of catalysts is necessary for the reactions to proceed. The activators include metal catalysts, electrophiles such as Br^+, Cl^+, I^+, RSe^+, and strong acids. Of the various activation types, metal-based catalytic systems are more preferred, because it is relatively easy to develop enantioselective variants using a combination of metals and chiral ligands.

In the middle of the last century, organic chemists began to use mercury salts for the addition of H—X nucleophiles onto C—C multiple bonds. The toxicity of mercury compounds and the problems associated with their handling, disposal and demercuration in a subsequent step make the use of mercury salts unsuitable for modern, sustainable organic synthesis. In recent years, the area has witnessed a tremendous growth and there has been a resurgence of interest in the addition of pronucleophiles (X—H) across unactivated C—C multiple bonds.[1] However, almost all of them are limited in scope (with respect to either C—C bonds, metals or nucleophiles) and very general in content. Moreover, most of the processes covered in various reviews employ starting materials containing C—C multiple bonds bearing nucleophiles in the tether, which on treatment with metal catalysts trigger a cascade leading to the formation of carbo- or heterocycles.[2] It would be beneficial for synthetic organic chemists to the literature exclusively on the addition of various nucleophiles to unactivated carbon—carbon multiple bonds. In this review, we intend to comprehensively summarize the transition metal (Groups 4—12)-catalyzed reactions covered in the literature from January 2000 to April 2011. For the sake of completeness, however, a few representative reports that have appeared earlier than January 2000 are also included. It should be noted that the reactions catalyzed by lanthanides/actinides[3] and the cascade reactions triggered by the addition of nucleophiles to C—C multiple bonds[2] are beyond the scope of this review. In this review, the transition metal-catalyzed reactions in which addition of X—H bonds across unactivated C—C multiple bonds takes place to generate XC—CH bonds are only described. The examples of C—C multiple bonds include alkenes, allenes, and alkynes and the examples of nucleophiles include carbon, nitrogen, and oxygen.

2. Addition of carbon nucleophiles to C—C multiple bonds

The additions of carbon nucleophiles onto carbon—carbon multiple bonds are of great interest to the synthetic community. A number of approaches to the addition of C-nucleophiles to unactivated alkynes, allenes, and olefins have been explored in the 20th century, including thermal,[4] free radical-mediated,[5] and Lewis[6] and Brönsted acid[7]-catalyzed processes. These processes were, however, limited to the point of being only marginally useful and most of them have some limitations such as harsh reaction conditions, poor functional-group compatibility, and requirement of a stoichiometric amount of base. Recently, transition metal catalysts represent a potential method for the addition of stabilized carbon nucleophiles onto carbon—carbon multiple bonds under mild conditions.

2.1. Addition onto alkynes

2.1.1. Intramolecular reactions. In 1991, Balme and co-workers reported the first example of intramolecular transition metal-catalyzed addition of C-nucleophiles on unactivated alkynes.[8] They observed that the cyclization of alkynes bearing active methines proceeded in the presence of 10 mol % Pd(dppe) and 20 mol % ^{t}BuOK to afford products in moderate yields (Scheme 1a). Later, in 1997, Tsukada and Yamamoto reported efficient and mild conditions that do not require any external base for similar transformations. For instance, 5 mol % $Pd(OAc)_2$ and 20 mol % cod in toluene/ethanol at 70 °C afforded the cyclized products (Scheme 1b).[9] A similar type of reaction, commonly referred to as a Conia-ene reaction, reported in 1968, involves the intramolecular cyclization of an alkynyl β-ketoester (Scheme 1c).[10] The reaction was known to proceed at very high temperatures (up to 250 °C), and the first metal-catalyzed version of this reaction was developed in 1983 by Conia and co-workers using $HgCl_2$ in strongly acidic media.[11] Recent research reveals that the use of transition metal catalysts is an efficient means for effecting this transformation under mild reaction conditions.

Toste and co-workers developed a Au(I)-catalyzed Conia-ene reaction of alkynyl β-ketoesters **1** that proceeds at room temperature (Table 1).[12] This method provides an efficient means for synthesis of *exo*-methylenecycloalkanes **2** with high