



Cross coupling reactions of multiple C–Cl bonds of polychlorinated solvents with Grignard reagent using a pincer nickel complex

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ABSTRACT

The nickel(II) complex of a bulky pincer-type ligand, N,N'-bis(2,6-diisopropylphenyl)-2,6-pyridinedicarboxamido, was examined for sp^2 – sp^3 coupling of Grignard reagents with polychlorinated solvents. The nickel(II) complex catalyzed C–C coupling of polychlorinated alkyl halides, such as dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4), with various Grignard reagents. The effective activation of multiple C–Cl bonds proceeded under ambient reaction conditions and within a short time (20 min). This catalyst displays the highest activity yet reported for this reaction type, with catalyst loading as low as 0.4 mol% and turnover frequency (TOF) as high as 724 h^{-1} . The catalyst is capable of replacing all chlorine atoms with C–C bond formations for all of the polychlorinated solvents under investigation. The catalytic process could prove to be an efficient method of remediation of toxic polychlorinated solvents while generating synthetically and commercially important chemicals.

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1. Introduction

Transition metal catalyzed C–C coupling of organometallic reagents with organic electrophiles is growing into a prominent area of research in synthetic chemistry [1,2]. Broad applicability, catalyst availability and high selectivity are major characteristics, which fuel advancements in transition-metal-catalyzed cross couplings of halogenated organic molecules with organometallic nucleophiles [3]. Chlorinated organic molecules including polychlorinated solvents continue to be broadly produced and used in megaton quantities worldwide, for diverse applications in industry and research. Owing to the ease of availability, their use as synthetic feedstock for high value chemicals and products provides a potentially valuable synthetic process. This can not only serve as an alternative to the traditional disposal of these chlorinated solvents, but also leads to the generation of relatively less toxic valuable chemicals.

Nickel [4–19] and palladium [20,21] metal salts, their various complexes or solid-supported systems, have been applied as catalysts to accomplish C–C bond formation between Grignard reagents and activated organic halides. However, current methods to accomplish this Kumada–Corriu type coupling extend limited

utility to unactivated alkyl halides [22–27]. This may be due to the complexity of alkyl halides, especially those with β -hydrogen atoms, which represent a more difficult class of electrophiles for cross-coupling reactions than the corresponding vinyl or aryl halides. In addition, successes in the cross-coupling of alkyl halides has been limited due to their tendency to participate in competitive side reactions and inability to undergo oxidative addition [19]. Beside these problems, an efficient activation of multiple C–Cl bonds such as in polychlorinated solvents remains a prohibitive challenge. Only few research groups have accomplished coupling of di or polychloroalkanes with organometallic nucleophiles to form C–C bond via sp^2 – sp^3 coupling [28–31]. The insertion of carbene precursor into an aliphatic carbon–halogen bond (polychlorinated alkane) using silver(I) complex of a fluorinated tris(pyrazolyl)borate ligand [28] was previously reported in the formation of new sp^2 – sp^3 C–C bond. This catalyst activated only one C–Cl bond, while all remaining carbon bound chlorines were undisturbed. Amongst the successful reports of the activation of C–Cl bonds of a carbon center in a polychlorinated alkane, the activation of multiple C–Cl bonds is still quite limited [29,30]. A P-functionalized aminopyridine ligand coordinated rhodium(I) complex was successfully applied in the activation of both C–Cl bonds of dichloromethane to form a μ -methylene bridged rhodium(III) complex as well as dimeric rhodium(III) complex with terminal chloromethyl groups [32]. Special mention may be made of a nickel pincer catalyst [29] for efficient activation of multiple C–Cl bonds in CH_2Cl_2 and $CHCl_3$, with highly selective C–C

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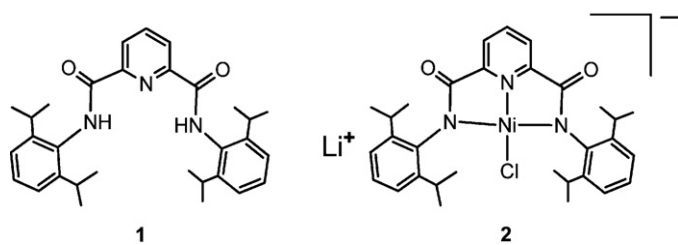


Fig. 1. N2, N6-bis (2, 6-diisopropylphenyl) pyridine-2, 6-dicarboxamide (**1**), its nickel(II) complex (**2**).

bond formation with Grignard reagents. Use of this nickel complex for activation of multiple C–Cl bonds in different polychloroalkanes has also been reported [31]. However, low reactivity and conversion along with often harsh and long reaction conditions are other problems associated to these previous reports.

Nickel complexes have been applied to accomplish both cross coupling of unactivated alkyl halides [20,21] and as efficient catalysts for Kumada–Corriu coupling when pincer ligands are utilized [29]. Metal complexes of pincer ligands possess unique structural and electronic properties leading to their utility in catalyzing several transformation reactions efficiently, including multiple C–Cl bonds activation and subsequent multiple C–C bonds formation. As reported previously, metal complexes of N,N,P- and N,N,N of amido–pincer ligands show higher activities over the metal complexes of P,N,P pincer ligand for C–C coupling [33]. Most pincer ligands can be easily synthesized with readily available starting materials, suggesting their use for metal complex catalysts may be economical.

The present study uses a pincer ligand based on a diamidopyridine ligand. The ligand (**1**, N2, N6-bis (2, 6-diisopropylphenyl) pyridine-2, 6-dicarboxamide) (Fig. 1) was previously reported to synthesize various metal complexes by Erker et al. [34]. The synthesis and characterizations of ruthenium and nickel complexes using the deprotonated form of the ligand (**1**) was reported, which were applied to accomplish ring closing metathesis reactions. The nickel complexes of this ligand (**1**) and analogous ligands have also been reported for efficient reaction with carbon dioxide and other small molecules or ligands [35,36]. No other uses or applications

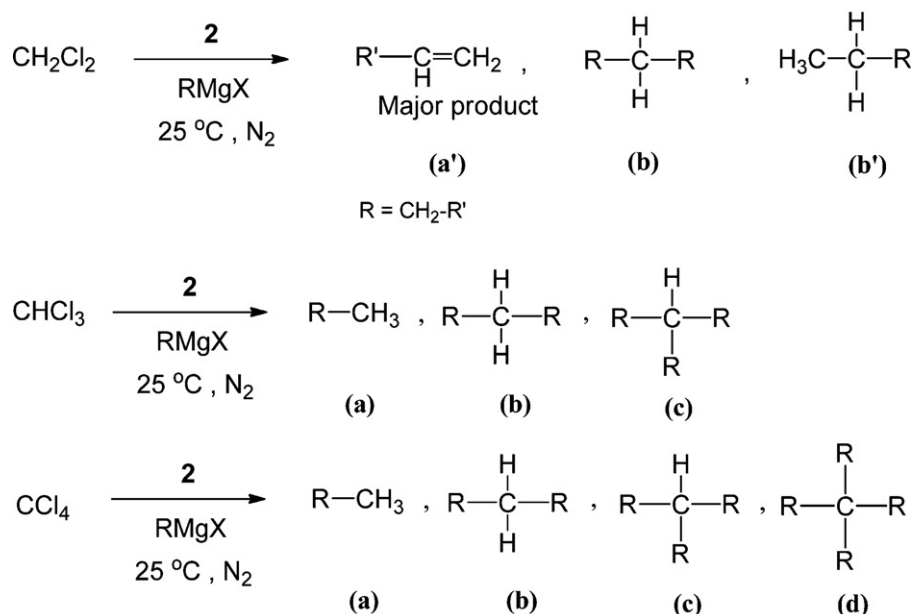
have been reported yet to expand the scope of utilization of this ligand and resulting complexes.

Here, we report in detail the catalytic cross-coupling of Grignard reagents with the polychlorinated solvents (Scheme 1) CH_2Cl_2 , CHCl_3 and CCl_4 using nickel(II) complex (**2**) of the pincer ligand (**1**) (Fig. 1). Cross couplings of polychlorinated solvents were accomplished with an array of alkyl, allyl and benzyl Grignard reagents, under ambient conditions. Interestingly, the catalyst can efficiently couple all the C–Cl bonds in every polychlorinated solvent used for this study with Grignard reagents to form C–C coupled products. The current study presents the first example of a catalyst system which is capable of catalyzing C–C cross-coupling reactions involving all the chlorine atoms of CH_2Cl_2 , CHCl_3 and CCl_4 . The catalyst showed a TOF of 463 h^{-1} and 724 h^{-1} when CH_2Cl_2 and CHCl_3 or CCl_4 were used as substrates. Such high catalytic activity, to the best of our knowledge, is the highest (5–10 times) for cross-coupling reactions involving polychlorinated molecules. Furthermore, this is the first report toward the successful cross-coupling of all the 4 C–Cl bonds of CCl_4 with Grignard reagents. The catalytic system described here could potentially be applied to efficiently decontaminate toxic polychlorinated solvents while generating value-added chemicals.

2. Experimental

2.1. Materials and methods

All the chemicals and solvents were obtained either from Aldrich Chemical Co., USA or Fisher Scientific Company, USA and used as obtained without further purifications unless otherwise stated. Tetrahydrofuran (THF), acetonitrile, hexanes, toluene, chloroform, and carbon tetrachloride were purified according to the literature procedure [37]. Anhydrous CH_2Cl_2 (sure seal) was used without further purification. Carbon tetrachloride was used in very small quantities and according to all pertinent regulations. ^1H and ^{13}C NMR spectra were obtained using a Bruker 600 MHz nuclear magnetic resonance (NMR) instrument. The spectra were collected at 25°C and chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) as an external standard unless otherwise stated. Infrared spectra were obtained on a Shimadzu FT-IR Affinity-1



Scheme 1. General scheme for the products formed in the cross coupling reaction of CH_2Cl_2 , CHCl_3 and CCl_4 with different Grignard reagents.

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