achieved. Although the NHCs are costly, they are not prone to oxidation or hydrolysis as are the cheaper alkylphosphines and phosphinites, phosphonites, or phosphites.

5.4 Cyclotrimerization Reactions of Alkynes
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5.4.1 Introduction

Transition metal-catalyzed or transition metal-mediated cyclotrimerization reactions have prospered since the rather serendipitous discovery by Berthelot and first systematic studies by Reppe of this highly useful synthetic methodology [251]. Especially the [2+2+2] cyclotrimerization of alkynes has matured into a valuable tool for the construction of complex organic molecules [252]. The last decade has seen growing application of traditional, often cobalt- or rhenium-based catalysts as well as the development and application of new catalyst systems, including chiral complexes, and extensive studies toward chemo-, regio-, and stereoselectivity. The experimental and theoretical results are regularly compiled and commented in reviews and book chapters [253]. The mechanistic details of the cyclotrimerization reaction were elicited by several computational studies, *inter alia* including the formation of pyridines from alkynes and nitriles, and will not be discussed in detail here [254]. This chapter will focus on the application of different catalyst systems for the preparation of interesting and useful molecules and molecular frameworks.

5.4.2 Most Commonly Used Metals as Catalysts in [2+2+2] Cycloadditions

5.4.2.1 Catalyst Systems

The most often and regularly applied catalyst systems for cyclotrimerization reactions are found on the right side of the periodic table, displaying the late transition metals. While with many metals examples for cyclotrimerization reactions have been described, only few of them find regular application. These catalysts are based on metal complexes of Ru, Co, Rh, Ir, and Ni. Especially the group 9 metals adopt a highly prominent role in the area of [2+2+2] cycloaddition reactions [255]. However, the nature of the applied catalyst systems within this transition metal group are very different between Co and Rh/Ir. Comparison of the reactivity of the metals in complexes with identical organic ligand framework as precatalysts for cyclotrimerizations demonstrated the largely different reactivities [256].