

## A new synthetic pathway towards cyaphide complexes

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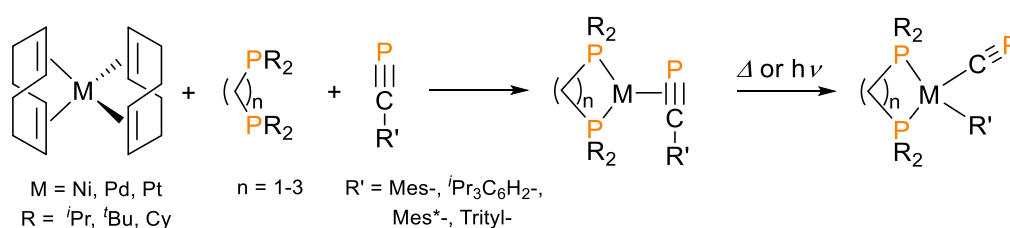
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Since the introduction of the first Pt(II)-cyaphide complex by Angelici *et al.* in 1992,<sup>[1]</sup> there have been many attempts to isolate cyaphide (C≡P<sup>-</sup>) complexes. In 2006, Grützmacher *et al.* reported on the first crystallographically characterized Ru(II) complex containing a terminally bound cyaphide ligand.<sup>[2]</sup> This was achieved by desilylation and rearrangement of an  $\eta^1$ -coordinated-silylphosphaalkyne. This method was adopted by several groups and led to a variety of similar transition metal-cyaphide complexes.<sup>[3-4]</sup> Unfortunately, none of these complexes undergo any consecutive reactions, due to the sterically demanding substituents on the co-ligands.

Jones *et al.* demonstrated that C(sp<sup>2</sup>)-C(sp) bonds of aryl-nitriles and aryl-alkynes can be activated by Ni(0)- and Pt(0)-complexes.<sup>[5]</sup> Based on the valence isoelectronic relationship between nitriles and phosphoalkynes, we synthesized and characterized a selection of  $\eta^2$ -phosphoalkyne complexes of different low-valent transition metals bearing chelating diphosphine ligands (Scheme 1). The isolated M(0)  $\pi$ -complexes were then reacted under various conditions (thermal, photochemical or Lewis acid promoted activation) to achieve C-C≡P-bond activation, forming the desired M(II)  $\sigma$ -cyaphide complexes by oxidative addition. The obtained cyaphide complexes, were then subjected to consecutive reactions to prove the existence of the cyaphide moiety.



Scheme 1: Synthesis and activation of transition-metal-phosphoalkyne complexes.

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