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## Nickel-Catalyzed Synthesis of Diaryl Carbonates from Phenols and Carbon Monoxide

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Diaryl carbonate is an important class of molecule as a key motif of commercial polycarbonates. In this work, we report nickel-mediated dehydrogenative carbonylative coupling of phenols. To circumvent deactivation of a nickel catalyst by coordination of carbon monoxide, we employed amine-promoted decarbonylation of phenyl formate<sup>1,2</sup> for generation of carbon monoxide and phenol *in situ*. Consequently, we successfully developed catalytic dehydrogenative coupling between a phenol and a phenyl formate which release carbon monoxide and another equivalent of phenol with the aid of triethylamine.

We commenced our study by pressurizing carbon monoxide to a solution of a nickel hydride complex prepared by oxidative addition of phenol to Ni(0) (Scheme 1). The reaction delivered diphenyl carbonate as a sole organic product along with quantitative formation of  $PCy_3Ni(CO)_3$ . By following our previous successful example to develop catalytic carbonylation using nickel, we treated a mixture of phenol and phenyl formate with nickel catalyst and triethylamine additive to promote decomposition of phenyl formate into phenol and carbon monoxide in situ (Scheme 2). As a result, we obtained desired diphenyl carbonate in 67% yield by using 1 equiv. of triethylamine as an additive.



Scheme 2. Catalytic carbonylation of phenol using phenyl formate

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