

# SYNLETT

## Spotlight 117

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

### Nickel Acetyl Acetonate [Ni(acac)<sub>2</sub>]

Compiled by Ambuja Pande

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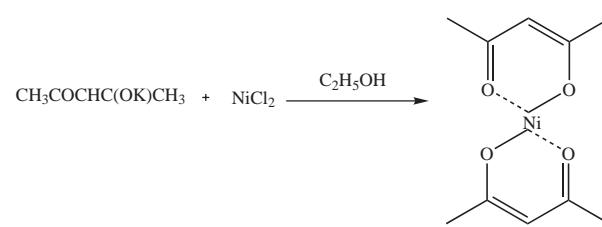
### Introduction

Nickel acetyl acetonate is also known as bis(acetylacetato) nickel(II). It has been used as a catalyst for oligomerization, telomerization, hydrosilylation, reduction, cross-coupling, oxidation, conjugate addition, addition to

multiple bonds and rearrangement reactions. It is a pale green solid ( $mp = 240\text{ }^{\circ}\text{C}$ ) that is soluble in ethers and aromatic and halogenated hydrocarbons.

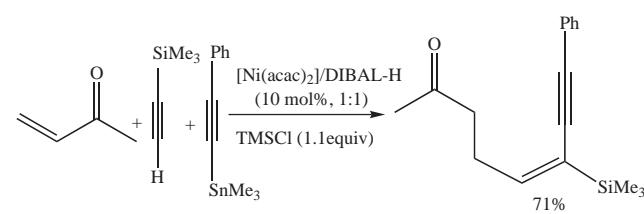
### Preparation

$\text{Ni}(\text{acac})_2$  is commercially available. Alternatively, it can be prepared from potassium acetylacetone and nickel(II) chloride by stirring for 30 minutes at room temperature in absolute ethanol.<sup>1</sup>

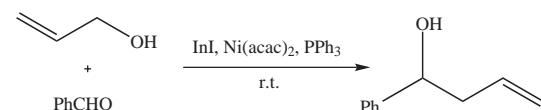


### Abstracts

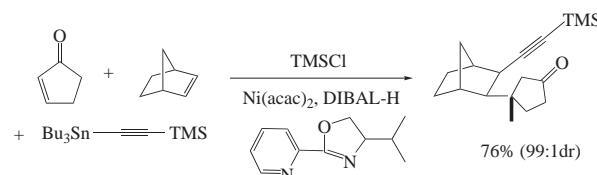
(A)  $\text{Ni}(\text{acac})_2$ -catalyzed couplings of enones, alkynes and main-group organometallic reagents generate acyclic structures in an efficient manner. Ikeda et al. produced conjugated enynes from acetylenic tin reagents.<sup>2,3</sup>



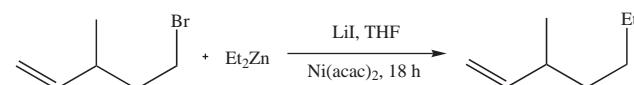
(B)  $\text{Ni}(\text{acac})_2$  is used in  $\text{InI}$ -mediated direct allylation of carbonyl compounds with allylic alcohols.<sup>4</sup> The reaction proceeded smoothly with catalytic amounts of  $\text{Ni}(\text{acac})_2$  and  $\text{PPh}_3$  to give the corresponding homoallylic alcohols in high yields.<sup>5</sup>



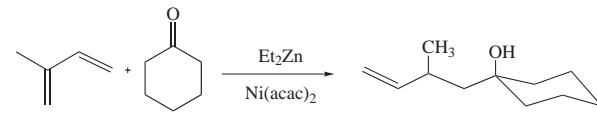
(C) Intermolecular coupling of an electron-deficient olefin with a strained olefin using  $\text{Ni}(\text{acac})_2$  and a modified chiral monodentate oxazoline provides good yields and enantioselectivity.<sup>6,7</sup>



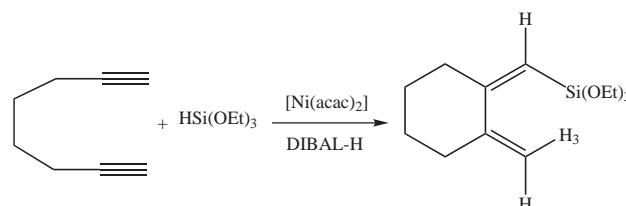
(D)  $\text{Ni}(\text{acac})_2$ -catalyzed cross-coupling between two  $\text{sp}^3$  carbon centers allows the synthesis of polyfunctional products.<sup>8</sup>



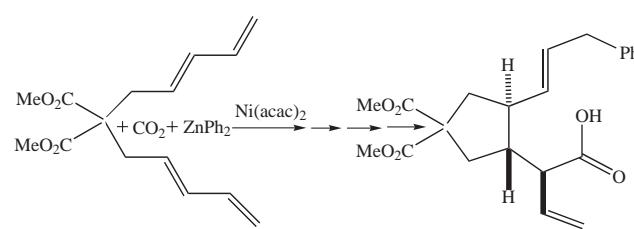
(E)  $\text{Ni}(\text{acac})_2$  promotes the coupling of alkenes with aldehydes in the presence of triethylborane or diethylzinc as reducing agents.<sup>9</sup> Triethylborane-mediated couplings work mainly for aromatic and unsaturated aldehydes, whereas diethylzinc-promoted couplings work best for aliphatic aldehydes and ketones. The reactions proceed well in water or in alcoholic solvents.<sup>10</sup>



(F)  $\text{Ni}(\text{acac})_2$ -assisted coupling of 1,7-diynes with silanes produces six-membered ring products with a *Z*-configured vinyl silane moiety.<sup>11</sup>



(G) Takimoto and Mori developed the  $\text{Ni}(\text{acac})_2$ -assisted coupling of 1,3-dienes,  $\text{CO}_2$ , and an organozinc reagent, allowing easy assembly of densely functionalized rings.<sup>12</sup> Terao et al. developed comparable multi-component coupling of two dienes, a silyl chloride, and a Grignard reagent.<sup>13</sup> The procedure has been extended to asymmetric variants.<sup>14</sup>



## References

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