

# SYNLETT Spotlight 117

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

Compiled by Ambuja Pande

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

Ambuja Pande was born in 1979. She received her B.Sc. Chemistry (Honours) degree in (2000) and M.Sc. Organic Chemistry degree (2002) from Kurukshetra University, Kurukshetra, India. She joined the D.R.D.E. in 2002 as a JRF and is currently pursuing her Ph.D. under the guidance of Dr. R. C. Malhotra, Joint Director of DRDE. Her present research is focused on irritants, both synthesis and application aspects.

Synthetic Chemistry Division, Defence Research and Development Establishment, Gwalior (M.P.) 474002, India  
E-mail: ambuja\_pande@rediffmail.com



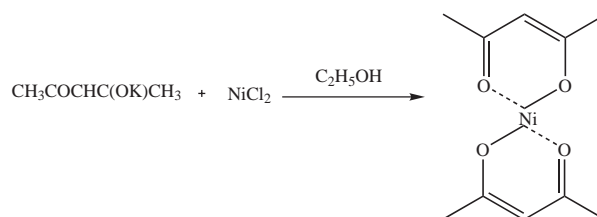
### Introduction

Nickel acetyl acetonate is also known as bis(acetylacetonato) 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 °C) that is soluble in ethers and aromatic and halogenated hydrocarbons.

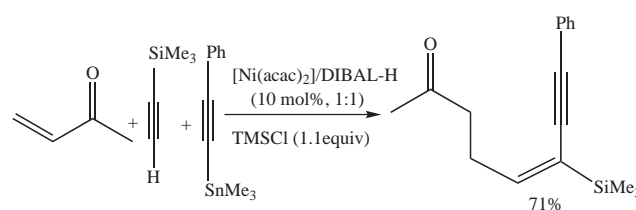
### Preparation

Ni(acac)<sub>2</sub> is commercially available. Alternatively, it can be prepared from potassium acetylacetonate and nickel(II) chloride by stirring for 30 minutes at room temperature in absolute ethanol.<sup>1</sup>

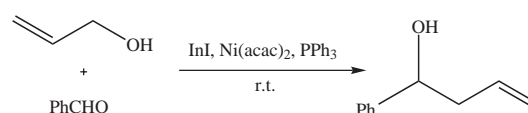


### Abstracts

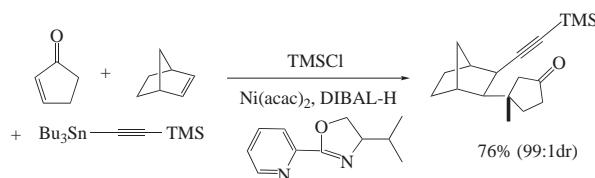
(A) Ni(acac)<sub>2</sub>-catalyzed couplings of enones, alkynes and main-group organometallic reagents generate acyclic structures in an efficient manner. Ikeda et al. produced conjugated enynes from acetylenic tin reagents.<sup>2,3</sup>



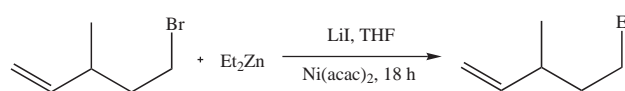
(B) Ni(acac)<sub>2</sub> is used in InI-mediated direct allylation of carbonyl compounds with allylic alcohols.<sup>4</sup> The reaction proceeded smoothly with catalytic amounts of Ni(acac)<sub>2</sub> and PPh<sub>3</sub> to give the corresponding homoallylic alcohols in high yields.<sup>5</sup>



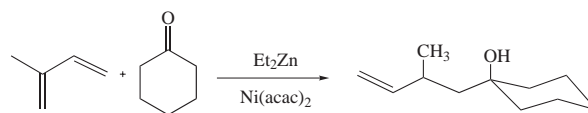
(C) Intermolecular coupling of an electron-deficient olefin with a strained olefin using  $\text{Ni}(\text{acac})_2$  and a modified chiral monodentate oxazoline provides good yields and enantioselectivity.<sup>6,7</sup>



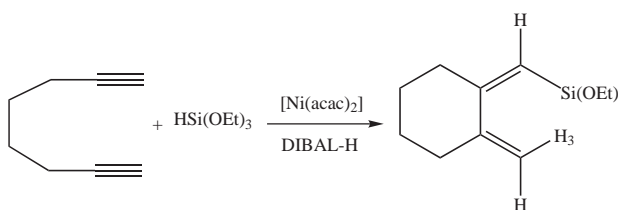
(D)  $\text{Ni}(\text{acac})_2$ -catalyzed cross-coupling between two  $\text{sp}^3$  carbon centers allows the synthesis of polyfunctional products.<sup>8</sup>



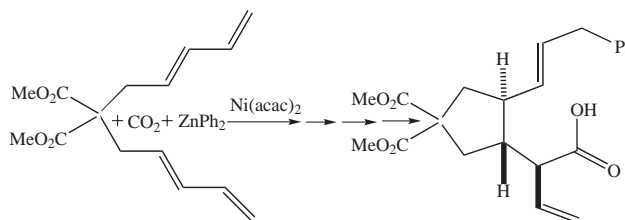
(E)  $\text{Ni}(\text{acac})_2$  promotes the coupling of alkenes with aldehydes in the presence of triethylborane or diethylzinc as reducing agents.<sup>9</sup> Triethylborane-mediated couplings work mainly for aromatic and unsaturated aldehydes, whereas diethylzinc-promoted couplings work best for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

- (1) Canoira, L.; Rodriguez, J. G. *J. Heterocycl. Chem.* **1985**, *22*, 1511.
- (2) (a) Ikeda, S.; Sato, Y. *J. Am. Chem. Soc.* **1994**, *116*, 5975. (b) Ikeda, S.; Kondo, K.; Sato, Y. *J. Org. Chem.* **1996**, *61*, 8248. (c) Ikeda, S.; Miyashita, H.; Taniguchi, M.; Kondo, H.; Okano, M.; Sato, Y.; Odashima, K. *J. Am. Chem. Soc.* **2002**, *124*, 12060. (d) Ikeda, S.; Cui, D. M.; Sato, Y. *J. Org. Chem.* **1994**, *59*, 6877. (e) Cui, D. M.; Tsuzuki, T.; Miyake, K.; Ikeda, S.; Sato, Y. *Tetrahedron* **1998**, *54*, 1063.
- (3) Ikeda, S.; Kondo, K.; Sato, Y. *Chem. Lett.* **1999**, 1227.
- (4) Hirashita, T.; Kambe, S.; Tsuji, H.; Omori, H.; Araki, S. *J. Org. Chem.* **2004**, *69*, 5054.
- (5) Loh, T. P.; Song, H. Y.; Zhou, Y. *Org. Lett.* **2002**, *4*, 2715.
- (6) Cui, D. M.; Yamamoto, H.; Ikeda, S.; Hatano, K.; Sato, Y. *J. Org. Chem.* **1998**, *63*, 2782.
- (7) Ikeda, S.; Cui, D. M.; Sato, Y. *J. Am. Chem. Soc.* **1999**, *121*, 4712.
- (8) Devasagayaraj, A.; Studemann, T.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2723.
- (9) Kimura, M.; Fujimatsu, H.; Ezoe, A.; Shibata, K.; Shimizu, M.; Matsumoto, S.; Tamaru, Y. *Angew. Chem. Int. Ed.* **1999**, *38*, 397.
- (10) Kimura, M.; Ezoe, A.; Tanaka, S.; Tamaru, Y. *Angew. Chem. Int. Ed.* **2001**, *40*, 3600.
- (11) (a) Suginome, M.; Matsuda, T.; Ito, Y. *Organometallics* **1998**, *17*, 5233. (b) Montgomery, J. *Angew. Chem. Int. Ed.* **2004**, *43*, 3890.
- (12) Takimoto, M.; Mori, M. *J. Am. Chem. Soc.* **2002**, *124*, 10008.
- (13) Terao, J.; Matsuo, S.; Shibata, K.; Tamaru, Y. *Angew. Chem. Int. Ed.* **1999**, *38*, 3386.
- (14) Takimoto, M.; Nakamura, Y.; Kimura, K.; Mori, M. *J. Am. Chem. Soc.* **2004**, *126*, 5956.