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)₂]

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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)₂ 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.¹

Abstracts

(A) Ni(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.^{2,3}

(B) Ni(acac)₂ is used in InI-mediated direct allylation of carbonyl compounds with allylic alcohols.⁴ The reaction proceeded smoothly with catalytic amounts of Ni(acac)₂ and PPh₃ to give the corresponding homoallylic alcohols in high yields.⁵

(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.^{6,7}

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

(E) $\text{Ni}(\text{acac})_2$ promotes the coupling of alkenes with aldehydes in the presence of triethylborane or diethylzinc as reducing agents.⁹ 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.¹⁰

(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.¹¹

(G) Takimoto and Mori developed the $\text{Ni}(\text{acac})_2$ -assisted coupling of 1,3-dienes, CO_2 , and an organozinc reagent, allowing easy assembly of densely functionalized rings.¹² Terao et al. developed comparable multi-component coupling of two dienes, a silyl chloride, and a Grignard reagent.¹³ The procedure has been extended to asymmetric variants.¹⁴

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