

SYNLETT Spotlight 150

Palladium(II) Acetate [Pd(OAc)₂]: A Versatile Catalyst

Compiled by Rakesh Kumar Vats



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

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Introduction

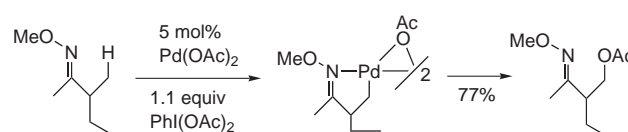
Palladium(II) acetate [Pd(OAc)₂] [CAS: 3375-31-3] is a commercially available reagent, which is stable and soluble in organic solvents. It has a melting point of 195 °C (dec.). It can be prepared from metallic palladium by dissolving in acetic acid containing nitric acid. It may contain nitrate anion as impurity. Pd(OAc)₂ is purified by dissolving it in hot benzene and concentrating the benzene solution after removing the insoluble part. Pure Pd(OAc)₂ can be obtained as needle-like crystals by recrystallization.

Palladium(II) acetate is used for oxidative addition, insertion, transmetalation and reductive elimination reactions. It is used for allylic oxidation (acetoxylation), e.g. oxidation of cyclohexene to 2-acetoxycyclohexene. Unsaturated aldehydes can be elongated by one carbon atom. Silyl enols undergo transmetalation followed by intramolecular alkene insertion and β -elimination. Acetoxycyclohexene is

prepared by reaction of benzene with Pd(OAc)₂. This is a useful method for phenol production from benzene. Pd(OAc)₂ is widely used in the presence of phosphine ligand and as a base in Heck reaction, for coupling aryl or vinyl halides with alkenes.¹ In the presence of TBAB, it catalyses direct homocoupling of aryl halides.² It is also used to improve Wacker oxidation of terminal alkenes to 2-alkanones with *p*-benzoquinone, which improves the reaction rate 50-fold.³ It is efficient in ligandless Suzuki cross-coupling of aryl boronic acids with aryl iodides.⁴ A stoichiometric quantity is required in Buchwald–Hartwig reaction of C–N bond formation. Selective reduction of alkynes is catalyzed by Pd(OAc)₂ with NaOMe⁵ and reduction of aryl/enol triflates by this catalyst is reported.⁶ Pd(OAc)₂ was microencapsulated in polyurea for making it reusable and recoverable catalyst for hydrogenation.⁷

Abstracts

(A) Oxygenation of unactivated sp³ C–H bonds can be achieved with Pd(OAc)₂ and PhI(OAc)₂ as oxidant. The unactivated sp³ C–H bonds of both oxime and pyridine substrates undergo highly regio- and chemoselective oxygenation.⁸



(B) Preparation of benzolactams by Pd(OAc)₂ catalyzes direct aromatic carbonylation in an atmosphere of CO gas with air.⁹

