

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

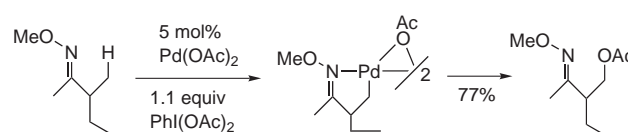
Palladium(II) acetate [Pd(OAc)₂] [CAS: 3375-31-3] is a commercially available reagent, which is stable and soluble in organic solvents. It has a melting point of 195 °C (dec.). It can be prepared from metallic palladium by dissolving in acetic acid containing nitric acid. It may contain nitrate anion 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

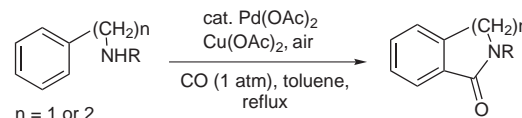
prepared by reaction of benzene with Pd(OAc)₂. This is a useful method for phenol production from benzene. Pd(OAc)₂ is widely used in the presence of phosphine ligand and as a base in Heck reaction, for coupling aryl or vinyl halides with alkenes.¹ In the presence of TBAB, it catalyses direct homocoupling 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

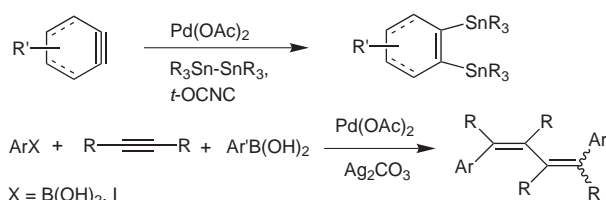


(B) Preparation of benzolactams by Pd(OAc)₂ catalyzes direct aromatic carbonylation in an atmosphere of CO gas with air.⁹



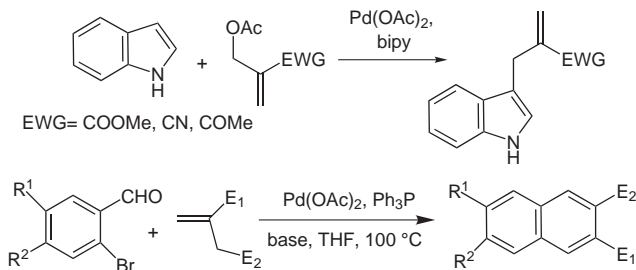
(C) Distannylation of strained C–C triple bonds is catalyzed by Pd(OAc)₂. Oxidative addition of a distannane to a palladium complex occurs during the distannylation of in situ generated arynes with distannanes in the presence of catalytic amount of Pd/*tert*-octyl isocyanide (*t*-OcNC) complex to give 1,2-distannylarenes in moderate to high yields.¹⁰

The synthesis of highly substituted 1,3-butadienes by arylation of internal alkynes can be achieved with the help of Pd(OAc)₂.¹¹

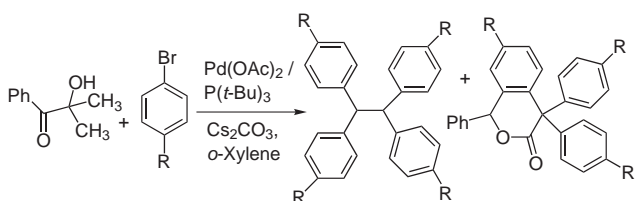


(D) Pd(OAc)₂-catalyzed functionalization of indoles with 2-acetoxy methyl substituted electron deficient alkenes was performed under neutral conditions. This protocol is very efficient and may open new area for functionalization of indoles.¹²

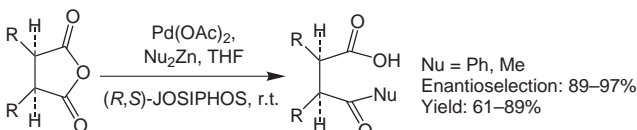
Pd(OAc)₂-catalyzed tandem Heck and aldol reaction between 2-bromobenzaldehyde and functionalized alkenes leads to naphthalene.¹³



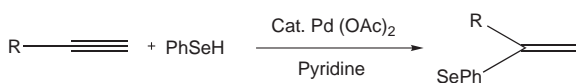
(E) Pd(OAc)₂ catalyzes multiple arylation via successive C–C and C–H bond cleavages. These unprecedented reactions seem to provide useful information for designing new catalytic cycles that occur via C–C and C–H cleavages.¹⁴



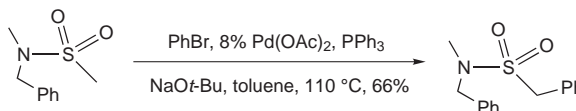
(F) The asymmetric desymmetrization of prochiral meso compounds represents a powerful strategy for the expedient synthesis of two or more contiguous stereogenic centres in one operation. Pd(OAc)₂ provides the desired keto acid in good yield and enantioselective excess.¹⁵



(G) Pd(OAc)₂ in pyridine is developed as an effective catalyst for highly regioselective hydroselenation of alkynes.¹⁶



(H) The α -arylation of methanesulfonamides using phosphine ligands and NaOt-Bu as a base was also achieved with Pd(OAc)₂.¹⁷



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