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# Communications

## Stereoselective Hydrogenation of Alkynes, Enynes, and Dienes by Interlamellar Montmorillonite–Diphenylphosphinepalladium(II) Complex[†]

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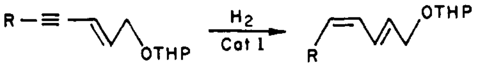
*Summary:* Stereoselective hydrogenation of alkynes, enynes, and dienes catalyzed by a heterogenized homogeneous catalyst, interlamellar montmorillonite–diphenylphosphinepalladium(II) anchored complex,[1] has been reported.

*Sir:* Stereoselective semihydrogenation of alkynes and enynes is of current interest.[2] The direct use of this selectivity in organic synthesis is to introduce functionality and stereochemistry simultaneously in the synthesis of natural products, especially biologically active compounds such as carbohydrates,[3] leukotrienes,[4] pheromones,[5] and prostaglandins.[6]

We earlier synthesized and characterized interlamellar montmorillonite–diphenylphosphinepalladium(II) chloride complex (I) and evaluated for hydrogenation of alkynes and alkenes, which was found to display more activity than the analogous polymer-bound complex, and the rate is consistent for several recycles.[1] We present in this paper the stereoselective hydrogenation of alkynes, enynes, and dienes in excellent yields by the catatlyst I (Table I).

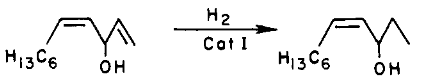
Catalyst I was prepared as reported earlier.[1] Hydrogenation reactions were carried out under very mild conditions in a 100-mL flask. Catalyst I (0.048 mM of Pd) was pretreated in THF (6 mL) with hydrogen at room temperature and atmospheric pressure in a classical hydrogenation apparatus for 15 min, substrate (4.8 mM) was then introduced, and hydrogenation was conducted until the theoretical volume of gas has been absorbed (5–20 min). The catalyst was removed by simple filtration, and the reaction mixture was purified by column chromatography to yield pure product. All the products are identified and quantified by GLC comparison with known samples/$^1$H NMR spectroscopy.

Selective semihydrogenation is demonstrated in the hydrogenation of alkynes and conjugated enynes in excellent yields (eq 1, entries 1–8). The dienes in unconjugated systems are selectively hydrogenated to monoenes (eq 2, entries 9–11), but the hydrogenation is very sluggish in the conjugated diene system. The cis selectivity, envisioned in the semihydrogenation of triple bond in the varied systems such as simple alkynes of divergent substituents, for conjugated enynes is always >85% (entries 1–8). There is no overhydrogenation product. The high cis selectivity as described demonstrates versatility of the present catalytic system.

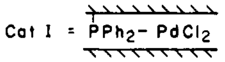


(eqn. 1)

R = $CH_3$ or $CH_2OTHP$



(eqn. 2)



Horizontal lines indicate montmorillonite interlayers.

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[†] RRL(H) Communication No. 2142.

(1) The complex Pd/P ratio is approximately 1:1. For synthesis and characterization, please see: Ravikumar, K.; Choudary, B. M.; Zafar Jamil; Thyagarajan, G. *J. Chem. Soc., Chem. Commun.* **1986**, 130.

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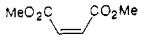
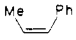
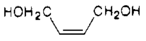
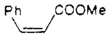
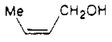
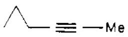
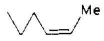
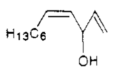
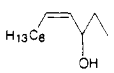
**Table I. Stereoselective Hydrogenation of Alkynes, Enynes, and Dienes**

| entry | substrate | product | cis selectivity, % (cat. I)[a,b] |
|---|---|---|---|
| | | Alkynes | |
| 1 | $MeO_2C$–≡–$CO_2Me$ |  | 97 |
| 2 | Ph–≡–Ph |  | 98 |
| 3 | Me–≡–Ph |  | 97 |
| 4 | $HOH_2C$–≡–$CH_2OH$ |  | 97 |
| 5 | Ph–≡–COOMe |  | 95 |
| 6 | Me–≡–$CH_2OH$ |  | 96 |
| 7 |  |  | 95 |
| | | Enynes | |
| 8 |  |  | |
| | | a: R = $CH_3$ | 87[c] (86)[d] |
| | | b: R = $CH_2OTHP$ | 85[c] (88)[d] |
| | | Dienes | |
| 9 |  |  | 85[c] |
| 10 |  |  | 99 |
| 11 |  |  | 95 |

[a] Yields at 100% conversion. [b] Yields by GC/NMR. [c] Isolated yields. [d] Yields by Lindlar catalyst.

In contrast, analogous polymer-bound palladium(II) complex,[7] and Lindlar[8] and rhodium cationic complex catalysts[9] are sensitive to the nature of the systems and substituents present in those systems. Analogous polymer-bound palladium(II) complex displays cis selectivity as low as 50% for aromatic-substituted alkynes and high selectivity for simple alkynes.[7] The widely used Lindlar catalyst and recently reported Pd/W have shown 94% maximum cis selectivity in the semihydrogenation of triple bond in simple alkynes.[2,8,10] The striking failure of the Lindlar catalyst (Pd/BaSo$_4$) is evident in the semihydrogenation of methylphenylpropiolate (entry 5), which gave primarily totally hydrogenated product.[9] The cis selectivity in the semihydrogenation of conjugated enynes by the catalyst I is comparable with the Lindlar as described in the Table I.

Although rhodium cationic complex exhibited the cis selectivity as high as 99%, in most of the cases it shows poor selectivity in the hydrogenation of butynediol[9] (entry 4). Further, the recovery of this complex from the reaction medium is difficult.

The other striking feature of the present catalytic system is that unconjugated dienes are selectively hydrogenated without undergoing isomerization. The terminal double bond is preferentially hydrogenated in presence of hindered double bond (entry 9).

Thus the results of stereoselectivity described in this paper are demonstratively comparable and project the present catalytic system as practical and viable alternative to the Lindlar, rhodium cationic complex, polymer-anchored palladium(II) complex, and Pd/W for syntheses of various biologically active compounds.

The $^{1}$H NMR data ($CDCl_3$, 300 MH$_z$) of the products for entries 8a, 8b, and 9 are as follows. 8a: $\delta$ 5.30–5.60 (m, 4 H), 5.05 (s, 1 H), 4.6 (d, 2 H), 3.9 (t, 2 H), 1.3–1.8 (m, 6 H), 1.58 (d, 3 H). 8b: $\delta$ 5.50–5.80 (m, 4 H), 4.90 (s, 2 H), 4.6 (d, 4 H), 3.50 (t, 2 H), 3.80 (t, 2 H), 1.2–1.8 (m, 12 H). 9: $\delta$ 5.25–5.7 (m, 2 H), 4.30 (m, 1 H), 2.10 (m, 2 H), 1.20–1.50 (m, 10 H), 0.9 (t, 6 H).

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# Novel Alkylation with Tetrathiotungstates and Tetrathiomolybdates: Facile Synthesis of Disulfides from Alkyl Halides

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*Summary:* A novel reaction of alkyl halides with piperidinium tetrathiotungstate or piperidinium tetrathiomolybdate ($MS_4^{2-}$) has been found to afford disulfides in good to excellent isolated yields under very mild reaction conditions.

*Sir:* Interest in sulfur-containing compounds of molybdenum and tungsten has grown with respect to their implications in bioinorganic chemistry and catalysis.[1,2] Although these thioanions,[3] organic ligand complexes,[4] and polymeric heteronuclear clusters[5] have been the subject

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