

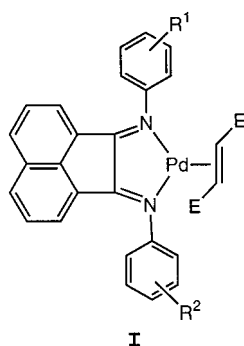
Selective Homogeneous Palladium(0)-Catalyzed Hydrogenation of Alkynes to (Z)-Alkenes**

Martijn W. van Laren and Cornelis J. Elsevier*

The selective semihydrogenation of alkynes to (Z)-alkenes seems to be a simple reaction, yet this type of conversion remains a desirable synthetic tool. A variety of catalysts is available for the conversion of alkynes into (Z)-alkenes; the best known and most efficient ones are heterogeneous catalysts such as the Lindlar catalyst,^[1] nickel boride,^[2] the "P2Ni" catalyst,^[3] and palladium immobilized on a clay.^[4] Especially the Lindlar catalyst suffers from a number of major problems in the selective *cis*-hydrogenation of alkynes, notably, partial isomerization of the (Z)-alkene product to the (E)-alkene, shift of the double bond, overreduction to the alkane, and problems with reproducibility. Only a few examples are known of homogeneous catalyst systems that show good selectivity for a wider range of substrates, for example, rhodium-^[5] and Cr(CO)₃-catalyzed hydrogenation.^[6] For palladium, however, few homogeneous catalyst systems are known, and these involve palladium(II) complexes.^[7, 8] The only homogeneous palladium(0) catalyst is the complex [Pd₂(dppm)₃], which shows low activity in the hydrogenation of propyne and 2-butyne.^[9]

Here we report the first example of a homogeneous palladium(0) catalyst bearing a bidentate nitrogen ligand that is able to homogeneously hydrogenate a wide variety of alkynes to the corresponding (Z)-alkenes with very high selectivity. Additionally, enynes are selectively converted into dienes.

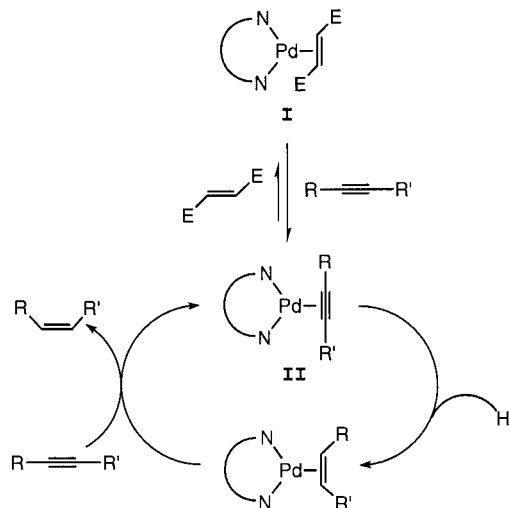
As part of our continuing interest in carbon–element (e.g., C–C, C–H, C–N, C–X) bond-forming reactions,^[10] we employed zerovalent palladium precatalysts **I**, which contain the rigid bidentate nitrogen ligand bis(arylimino)acenaphthene (bian). These have previously been isolated with an electron-



E = CO₂Me

- a:** R¹ = R² = 4-OCH₃
b: R¹ = 4-OCH₃; R² = 4-CH₃
c: R¹ = R² = 4-CH₃
d: R¹ = R² = 2,6-(CH₃)₂

deficient alkene as the ancillary ligand;^[11] however, analogues of **I** with electron-rich alkenes are not stable. We reasoned that since simple alkenes are expected to be readily substituted by alkynes, if alkynes were hydrogenated in the presence of molecular hydrogen, subsequent fast substitution by excess alkyne could give rise to a viable catalytic cycle (Scheme 1).



Scheme 1. Proposed catalytic cycle for hydrogenation of alkynes.

We conducted hydrogenation reactions of alkynes at 20 °C and 1 bar hydrogen pressure with initial sample concentrations of about 0.5 M in THF and 1 mol % of **1a** as precatalyst. With 3-hexyne (**1**) and 4-octyne (**3**), high stereoselectivity (>99.5%) for the formation of (Z)-3-hexene and (Z)-4-octyne was observed, and hydrogenation proceeded with excellent yield. Various other alkynes were then subjected to these hydrogenation conditions (Table 1).

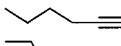
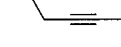
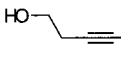
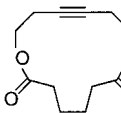
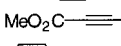
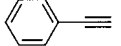
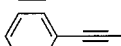
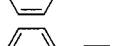
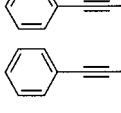
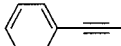
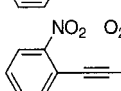
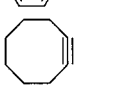
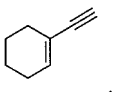
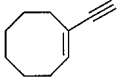
The stereoselectivity for the formation of the (Z)-alkene is generally excellent and in many cases superior to that obtained with Lindlar^[1] or P2Ni catalysts^[3] and comparable to or in several cases better than those of known homogeneous systems.^[5–7] Generally, quantitative conversion of the alkyne to the desired (Z)-alkene takes place, without concomitant alkane formation. The selectivity is highest (Z/E > 99/1) for simple alkynes such as **1** and **3**. The Lindlar catalyst gives 95/5 and 94/6 mixtures of Z/E alkenes, respectively, and only partial conversion in these cases.^[1c, d] Excellent results were also obtained for the homopropargylic alcohol **4**, alkynes with aryl- and/or electron-withdrawing substituents (**5–7**, **10**, **12**), and cyclooctyne (**13**). For **7** the stereoselectivity was determined by reaction with D₂. Semihydrogenation of **7** usually results in the formation of ethylbenzene; an 89/11 mixture of styrene/ethylbenzene was obtained at full conversion of **7**.^[1e]

Phenylacetylenes show somewhat lower but still very good selectivities, comparable to conversions with Lindlar or P2Ni catalysts, and for **8** and **9** only a small amount of alkane is formed. In several cases (**5**, **9**, **10**, **12**, **13**) some Z–E isomerization occurs, but only to a minor extent. Remarkably, no isomerization to (E)-stilbene was observed with **11**, whereas the amount of 1,2-diphenylethane is somewhat

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Table 1. Product distribution in the hydrogenation of alkynes with **1a** as precatalyst.^[a]

Substrate	Product distribution [%] ^[b]		
	(Z)-alkene	(E)-alkene	alkane
1 ^[c] 	> 99	–	–
2 ^[c] 	1-hexene exclusively		
3 	> 99	–	–
4 	> 99	–	–
5 	95	5	–
6 	> 98	< 1	< 1
7 	> 99 ^[d]	–	–
8 	92	2	6
9 	91	6	3
10 	95	5	–
11 	87	–	13
12 	97	3	–
13 	96	4	–
14 	ethynylcyclohexene exclusively		
15 	ethynylcyclooctene exclusively		

[a] Reaction conditions: 80 mm substrate and 0.8 mm precatalyst **1a** in THF at 20 °C and 1 bar H₂ pressure. [b] The reaction was monitored by GC analysis. The product distribution was determined by GC and ¹H NMR analysis at > 99.5% conversion of alkyne. [c] Hydrogenated with **1c** as precatalyst. [d] Determined by reaction with D₂.

higher than is obtained with Lindlar procedures; a 93/2/5 mixture of (Z)-alkene/(E)-alkene/alkane was reported.^[1f]

In the case of **1–6**, **10**, and **12** very little or no alkane is formed. The high selectivity in the case of dimethyl butynedioate (**6**) is noteworthy, as it indicates that hydrogenation of the Pd alkyne complex is faster than formation of the palladacycle with a second molecule of butynedioate, which is known to be a fast reaction.^[10b, 12] A Pd–alkyne complex similar to **II** was observed as an intermediate in the formation of such a palladacycle.^[10a, b]

Evidently, the hydrogenation of alkynes takes place with high chemoselectivity towards the triple bond. No hydrogenation of functional groups such as ester, carboxylic acid or nitro substituents has been observed, but **I** is capable of hydrogenating the carbon–carbon double bond in several cases. It was previously known that electron-deficient alkenes

can be hydrogenated with **I** as a precatalyst,^[13] but styrene and stilbene reacted sluggishly. In this context it is noteworthy that conjugated enynes such as **14** and **15** are cleanly (though in the case of **14** sluggishly) converted into the corresponding dienes by hydrogenation with **1a**, with no trace of hydrogenation of the double bond(s); hydrogen uptake stops completely after hydrogenation of the triple bond, without any decomposition of the catalyst. Employing a Lindlar catalyst with **14** led to significant overreduction (86/8/6 mixture of diene/ethylcyclohexene/ethynylcyclohexene) after uptake of one equivalent of H₂.^[14]

The effect of the substituents on the *N*-Ar moieties of **1** on the selectivity was briefly addressed for the hydrogenation of 1-phenyl-1-propyne (**8**; Table 2). The selectivity for (Z)-1-phenyl-1-propene decreases markedly with decreasing electron-donor character of the substituents on the *N*-aryl groups. For entries 1–3, the Z/E ratio decreases from 46 to 11, with a

Table 2. Product distribution in the hydrogenation of 1-phenyl-1-propyne to 1-phenyl-1-propene and 1-phenylpropane.

Entry	Precatalyst	Product distribution [%]		
		(Z)-alkene	(E)-alkene	alkane
1	1a	92	2	6
2	1b	85	5	10
3	1c	80	7	13
4	1d	62	3	35

concomitant increase of the amount of alkane formed. Especially the sterically congested complex **1d** (entry 4) exhibits a rather low selectivity and leads to formation of larger amounts of alkane. The latter result may be due to steric crowding, since **1d** may form a more stable complex with the (Z)-alkene than with the alkyne.

Use of zero-valent palladium catalyst precursors with other ligands—such as [Pd(dba)₂], [Pd(bpy)(alkene)], and [Pd(dab)-(alkene)] (Table 3)—leads to unstable complexes and/or

Table 3. Product distribution in the hydrogenation of 1-phenyl-1-propyne.

Entry	Precatalyst ^[a]	Product distribution (%)		
		(Z)-alkene	(E)-alkene	alkane
1	[Pd(dba) ₂]	70	8	22
2	[Pd(bpy)(dmfu)]	73	6	21
3	[Pd(dab)(dmfu)] ^[b]	–	–	–
4	[Pd(dppe)(dmfu)]	80	2	18
5	[Pd(bian)(dmfu)]	92	2	6

[a] bpy = bipyridyl, dab = *p*-anisylidiazabutadiene, dba = dibenzylideneacetone, dmfu = dimethyl fumarate, dppe = bis(diphenylphosphanyl)ethane. [b] The precatalyst decomposed almost immediately.

serious decomposition under the conditions employed. As a result, in these cases heterogeneous hydrogenation of **8** with low selectivity and a high degree of overreduction to *n*-propylbenzene was observed. The use of a complex containing a chelating biphosphane ligand such as dppe gives very stable alkyne and alkene complexes, and no decomposition is observed, but hydrogenation is very slow, and larger amounts of *n*-propylbenzene are formed. Thus, the selectivity of the Pd(bian) complexes **I** for hydrogenation of alkynes is much higher than those of the other precatalysts in Table 3.

The homogeneity of the hydrogenation was monitored by the addition of a tenfold excess of cyclohexene to the reaction mixture in several cases. Cyclohexene is not or only very slowly hydrogenated by homogeneous Pd species, but is readily hydrogenated by colloidal or heterogeneous Pd. As we did not observe the formation of any cyclohexane during the hydrogenation of the alkynes, it can be concluded that the Pd(bian)-catalyzed hydrogenation reaction is homogeneous.^[15]

The mechanism of this selective hydrogenation of alkynes is as yet unclear. The complexes **I** should be considered precatalysts, and the actual catalyst is probably a [Pd(bian)(alkyne)] complex **II** (Scheme 1). The stability of **II** relative to the corresponding alkene complex **I** is probably important for the observed chemoselectivity of hydrogenation. For most or all alkynes a high ratio **II/I** would be expected. Hydrogenation could readily take place by addition of hydrogen to **II** and subsequent insertion/elimination or by a pairwise transfer of hydrogen atoms. The latter was substantiated in similar hydrogenations by means of the *para*-hydrogen-induced polarization in ¹H and ²H NMR spectroscopy during hydrogenation.^[16] Currently, we are trying to extend the scope and to elucidate the mechanism of the reaction.

Experimental Section

Typical procedure for the catalytic hydrogenation of alkynes: **1a**^[11b] (25 mg, 0.04 mmol) and the alkyne (4.0 mmol) were added to 50 mL of dry THF in a Schlenk tube under nitrogen atmosphere. The solution was then subjected to a hydrogen atmosphere of 1 bar by first flushing with hydrogen and then slowly blowing hydrogen over the surface while the solution was vigorously stirred at 20 °C. The reaction was monitored by GC (Varian 3300; DB-5 column) and stopped when all alkyne had been consumed (conversion 99.5–100 %). The composition of the reaction mixture was determined by GC and ¹H NMR spectroscopic analysis.

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Self- and Directed Assembly of Hexaruthenium Macrocycles**

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Elegant work in the area of self-assembly by Stang,^[1] Lehn et al.,^[2] and many others^[3–7] has prompted our investigation of the potential to spontaneously construct Ru-based (macro)-molecules. More specifically, our goal involved the design and preparation of polyterpyridyl ligands that would form the basis of a “modular building block set”^[8] capable of being used to access “higher order” (fractal) architectures. Herein we report the construction of a bis(terpyridyl) monomer that facilitates the preparation of hexaruthenium macrocycles.

Linear bis(terpyridyl) monomers have been employed for the formation of layered polyelectrolyte films,^[9] Ru^{II}-based dendrimers,^[10] helical ligands,^[11] grids,^[12] racks,^[13] and photoactive molecular-scale wires,^[14] to mention but a few. Whereas progress in directed synthesis of cyclic rigid structures^[15] can be found in “shape-persistent” phenylacetylenes,^[16–18] diethynylbenzene macrocycles,^[19] and a hexagon containing 24 phenylene units,^[20] advances in self-assembly have yielded, for example, chiral^[21] and achiral circular

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