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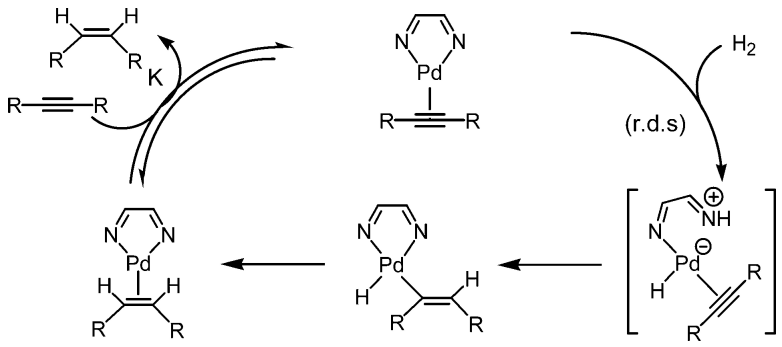

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Kinetic and Spectroscopic Studies of the [Palladium(Ar-bian)]-Catalyzed Semi-Hydrogenation of 4-Octyne

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Abstract: The kinetics of the stereoselective semi-hydrogenation of 4-octyne in THF by the highly active catalyst [Pd{(*m*,*m*′-$(CF_3)_2C_6H_3$)-bian}(ma)] (**2**) (bian = bis(imino)acenaphthene; ma = maleic anhydride) has been investigated. The rate law under hydrogen-rich conditions is described by $r = k$[4-octyne]$^{0.65}$[Pd]-[H_2], showing first order in palladium and dihydrogen and a broken order in substrate. Parahydrogen studies have shown that a pairwise transfer of hydrogen atoms occurs in the rate-limiting step. In agreement with recent theoretical results, the proposed mechanism consists of the consecutive steps: alkyne coordination, heterolytic dihydrogen activation (hydrogenolysis of one Pd−N bond), subsequent hydro-palladation of the alkyne, followed by addition of N−H to palladium, reductive coupling of vinyl and hydride and, finally, substitution of the product alkene by the alkyne substrate. Under hydrogen-limiting conditions, side reactions occur, that is, formation of catalytically inactive palladacycles by oxidative alkyne coupling. Furthermore, it has been shown that (*Z*)-oct-4-ene is the primary reaction product, from which the minor product (*E*)-oct-4-ene is formed by an H_2-assisted, palladium-catalyzed isomerization reaction.

Introduction

Homogeneous hydrogenation by transition metal complexes has played a key role in the fundamental understanding of catalytic reactions and has proven to be of great utility in practical applications.[1] Despite the wealth of information available for the homogeneous hydrogenation of carbon−carbon double bonds, remarkably few details have been reported for alkynes, even though a large number of catalysts have been tested and found active in this reaction.[2] Stereoselective semi-hydrogenation of carbon−carbon triple bonds is a highly desired tool for synthetic organic chemistry, and many of the products obtained through this reaction are useful in the synthesis of natural products, such as biologically active compounds. For such compounds, the stereo- and regiocontrol of the resulting double bond is essential for its biological activity. The most widely applied catalyst for the hydrogenation of alkynes to afford (*Z*)-alkenes employs group 8 transition metals of which the Lindlar catalyst (lead-poisoned Pd on $CaCO_3$) is the most prominent member.[3] This catalyst shows considerable selectivity for a wide variety of alkynes yielding the *cis*-alkenes, However, the formed *cis*-alkene is prone to *cis*-*trans* isomerization, bond-shift isomerization, and over-reduction under the reaction conditions. In addition, the Lindlar-catalyzed hydrogenation reaction suffers from low chemoselectivity and a low reproducibility, leading to product mixtures that need to be separated.[4]

Selective homogeneous hydrogenation of alkynes to the corresponding alkenes has been observed, for example, with ruthenium,[5] iridium,[6] chromium,[7,8] rhodium,[9] and iron[10] catalysts. However, only a few of these show a good selectivity and a reasonable activity toward a variety of alkynes containing different functional groups; therefore, the general application of these catalytic systems in synthetic organic chemistry remains rather limited. Moreover, most of the reported catalytically active systems deal with selective hydrogenation of terminal alkynes

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(1) Chaloner, P. A.; Esteruelas, M. A.; Joo, F.; Oro, L. A. In *Homogeneous Hydrogenation*; Ugo, R., James, B. R., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1993.
(2) Sanchez-Delgado, R. A.; Rosales, M. *Coord. Chem. Rev.* **2000**, 249−280.
(3) Hutchins, R. O.; Hutchins, M. G. K. In *Reduction of Triple-bonded Groups, The Chemistry of Functional Groups*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd.: New York, 1983; Vol. 1, pp 571−597.
(4) Ulan, J. G.; Maier, W. F. *J. Org. Chem.* **1987**, *52*, 3132−3142.
(5) (a) Albers, M. O.; Singleton, E.; Viney, M. M. *J. Mol. Catal.* **1985**, *33*, 77−82. (b) Albers, M. O.; Singleton, E.; Viney, M. M. *J. Mol. Catal.* **1985**, *30*, 213−217. (c) Blum, Y.; Czarkie, D.; Rahamim, Y.; Shvo, Y. *Organometallics* **1985**, *4*, 1459−1461. (d) Frediani, P.; Giannelli, C.; Salvini, A.; Ianelli, S. *J. Organomet. Chem.* **2003**, *667*, 197−208. (e) Schleyer, D.; Niessen, H. G.; Bargon, J. *New J. Chem.* **2001**, *25*, 423−426. (f) Suarez, T.; Fontal, B. *J. Mol. Catal.* **1988**, *45*, 335−344. (g) Bianchini, C.; Bohanna, C.; Esteruelas, M. A.; Frediani, P.; Meli, A.; Oro, L. A.; Peruzzini, M. *Organometallics* **1992**, *11*, 3837−3844.
(6) (a) Baddley, W. H.; Fraser, M. S. *J. Am. Chem. Soc.* **1969**, *91*, 3661−3663. (b) Navarro, J.; Sagi, M.; Sola, E.; Lahoz, F. J.; Dobrinovitch, I. T.; Katho, A.; Joo, F.; Oro, L. A. *Adv. Synth. Catal.* **2003**, *345*, 280−288. (c) Sanchez-Delgado, R. A.; Andriollo, A.; Gonzalez, E.; Valencia, N.; Leon, V.; Espidel, J. *J. Chem. Soc., Dalton Trans.* **1985**, 1859−1863.
(7) Sodeoka, M.; Shibasaki, M. *J. Org. Chem.* **1985**, *50*, 1147−1149.
(8) Sodeoka, M.; Shibasaki, M. *Synthesis* **1993**, *7*, 643−658.

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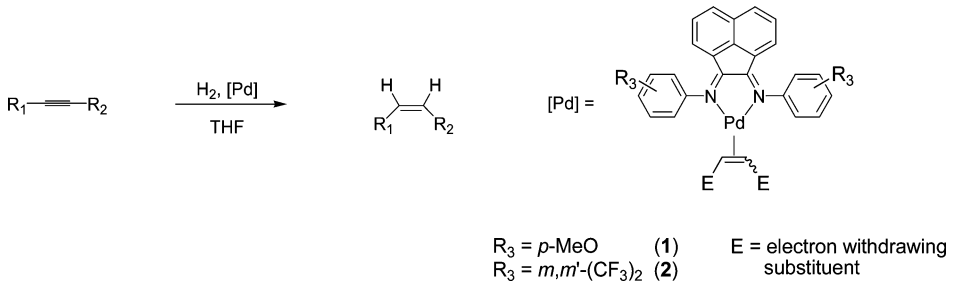
Scheme 1. Semi-Hydrogenation of Alkynes Catalyzed by [Pd(Ar-bian)(alkene)]



as the model substrates; hence, the stereoselectivity of the catalysts is not relevant and often not determined.

The number of homogeneous palladium systems that have been reported as active catalysts in the semi-hydrogenation of alkynes is still very limited. Most of these Pd catalysts are mononuclear palladium complexes, either Pd(II)[11] or Pd(0) complexes,[12] although some Pd clusters have also been found to be highly active in this type of hydrogenation reaction.[13] Considerable attention has been directed toward immobilized palladium complexes, where the palladium is coordinated to a ligand attached to a polymer, a clay, or other inorganic supports.[14]

In the past, some authors[12a] have reported a highly stereoselective hydrogenation of internal alkynes by zerovalent palladium catalysts bearing the rigid bidentate nitrogen ligand bis(*N*-arylimino)acenaphthene (Ar-bian), and which are able to homogeneously hydrogenate a wide variety of alkynes to form the corresponding (*Z*)-alkenes (Scheme 1). The observed selectivity toward the (*Z*)-alkene, using [Pd(4-MeO-C_6H_4-bian)(dmfu)] (**1**; dmfu = dimethyl fumarate) as the catalyst, is very high (>99%)[11a,c] for various alkynes under very mild conditions (25 °C, 1 bar H_2, see Scheme 1). Typical turnover frequencies (TOF) of 100−200 mol mol^{-1} h^{-1} were obtained with this catalyst. The high selectivity, that is in many cases superior to the one obtained with the Lindlar catalyst, is maintained until full conversion of the alkyne has been achieved (selectivity determined at >99.5% conversion). Under these conditions, both internal and terminal alkynes are reduced with great ease. Besides the high stereoselectivity, the chemoselectivity is also remarkably high as demonstrated by the presence of other reducible functional groups in the substrate (such as carboxy groups, nitro groups, or even alkene moieties in conjugated enynes), which remained unaffected under the hydrogenation conditions.

To elucidate the reaction mechanism, we report in this paper the investigation of the overall kinetics of the highly selective [Pd(Ar-bian)]-catalyzed semi-hydrogenation reaction, as well as NMR studies involving deuterium labeling and parahydrogen-induced polarization. Knowledge of the rate law was deemed essential to assign the rate-determining step in the putative cascade of elementary reaction steps.[15,16] We have specifically studied the semi-hydrogenation of 4-octyne employing the zerovalent precatalyst [Pd{(*m*,*m*′-$(CF_3)_2C_6H_3$)-bian}(ma)] (**2**; bian = bis(imino)acenaphthene; ma = maleic anhydride). The presence of electron-withdrawing groups on the Ar-bian ligand greatly enhances the rate of alkyne hydrogenation, while maintaining the high stereo- and chemoselectivity, which have typically been found for the [Pd(Ar-bian)] systems. A mechanism for the [Pd{(*m*,*m*′-$(CF_3)_2C_6H_3$)-bian}(ma)]-catalyzed semi-hydrogenation of 4-octyne is proposed in this article.

Results and Discussion

Preliminary Remarks. The synthesis of the precursor catalyst [Pd{(*m*,*m*′-$(CF_3)_2C_6H_3$)-bian}(ma)] (**2**) has been achieved by reacting the extremely versatile complex [Pd(nbd)(ma)] (**3**)[17] with the free ligand (*m*,*m*′-$(CF_3)_2C_6H_3$)-bian in THF (nbd = norbornadiene). This route has proven to be very successful for the synthesis of a wide variety of zerovalent palladium compounds, including the allegedly "unstable" [$Pd(N)_2$(ma)] complexes (where N is a simple "σ-donor-only" ligand). After workup, catalyst (**2**) is an air-stable compound; however, it was stored under nitrogen atmosphere to ensure its purity.

In a preliminary catalytic study, we found that the [Pd(Ar-bian)]-catalyzed hydrogenation of alkynes typically shows a distinct induction period, after which the alkyne consumption is linear with time. To obtain kinetic data from this reaction, the induction behavior during the first 10% of the alkyne conversion is disregarded, and only the alkyne consumption between 10 and 90% conversion is determined as a function of

(9) (a) Blum, J.; Rosenfeld, A.; Polak, N.; Israelson, O.; Schumann, H.; Avnir, D. *J. Mol. Catal. A* **1996**, *107*, 217−223. (b) Breuer, D.; Goen, T.; Haupt, H. J. *J. Mol. Catal.* **1990**, *61*, 149−162. (c) Cabeza, J. A.; Fernandez-Colinas, J. M.; Llamazares, A.; Riera, V. *J. Mol. Catal.* **1992**, *71*, L7−L11. (d) Candlin, J. P.; Oldham, A. R. *Discuss. Faraday Soc.* **1968**, *46*, 60−71. (e) Crabtree, R. H. *J. Chem. Soc., Chem. Commun.* **1975**, 647−648. (f) Crabtree, R. H.; Gautier, A.; Giordano, G.; Khan, T. *J. Organomet. Chem.* **1977**, *141*, 113−121. (g) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711−1732. (h) Stephan, M.; Kohlmann, O.; Niessen, H. G.; Eichhorn, A.; Bargon, J. *Magn. Res. Chem.* **2002**, *40*, 157−160.
(10) Bianchini, C.; Meli, A.; Peruzzini, M.; Frediani, P.; Bohanna, C.; Esteruelas, M. A.; Oro, L. A. *Organometallics* **1992**, *11*, 138−145.
(11) (a) Pelagatti, P.; Venturini, A.; Leporati, A.; Carcelli, M.; Costa, M.; Bacchi, A.; Pelizzi, G.; Pelizzi, C. *J. Chem. Soc., Dalton Trans*. **1998**, 2715−2721. (b) Costa, M.; Pelagatti, P.; Pelizzi, C.; Rogolino, D. *J. Mol. Catal. A* **2002**, *178*, 21−26.
(12) (a) van Laren, M. W.; Elsevier, C. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 3715−3717. (b) Sulman, E.; Deibele, C.; Bargon, *J. React. Kinet. Catal. Lett*. **1999**, *67*, 112−117. (c) van Laren, M. W.; Duin, M. A.; Klerk, C.; Naglia, M.; Rogolino, D.; Pelagatti, P.; Bacchi, A.; Pelizzi, C.; Elsevier, C. J. *Organometallics* **2002**, *21*, 1546−1553.
(13) (a) Cabeza, J. A. In *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raithby, P. R., Eds.; Wiley-VCH Verlag: Weinheim, Germany, 1999; Vol. 2, pp 715−740. (b) Evrard, D.; Groison, K.; Mugnier, Y.; Harvey, P. D. *Inorg. Chem.* **2004**, *43*, 790−796. (c) Niessen, H. G.; Eichhorn, A.; Woelk, K.; Bargon, J. *J. Mol. Catal. A* **2002**, *182*−*183*, 463−470.
(14) (a) Holy, N. L.; Shelton, S. R. *Tetrahedron* **1981**, *37*, 25−26. (b) Elman, B.; Moberg, C. *J. Organomet. Chem.* **1985**, *294*, 117−122. (c) Moberg, C.; Rakos, L. *J. Organomet. Chem.* **1987**, *335*, 125−131. (d) Choudary, B. M.; Sharma, G. V. M.; Bharathi, P. *Angew. Chem.* **1989**, *101*, 506−507. (e) Ferrari, C.; Predieri, G.; Tiripicchio, A.; Costa, M. *Chem. Mater.* **1992**, *4*, 243−245. (f) Islam, M.; Bose, A.; Mal, D.; Saha, C. R. *J. Chem. Res. (S)* **1998**, 44−45. (g) Michalska, Z. M.; Ostaszewski, B.; Zientarska, J.; Sobczak, J. W. *J. Mol. Catal. A* **1998**, *129*, 207−218.
(15) James, B. R. *Homogeneous Hydrogenation*; John Wiley and Sons: New York, 1973; pp 198−287.
(16) Wilkinson, F. *Chemical Kinetics and Reaction Mechanisms*; Van Nostrand Reinhold: New York, 1980, pp 65−130.
(17) Kluwer, A. M.; Elsevier, C. J.; Bühl, M.; Lutz, M.; Spek, A. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 3501−3504.

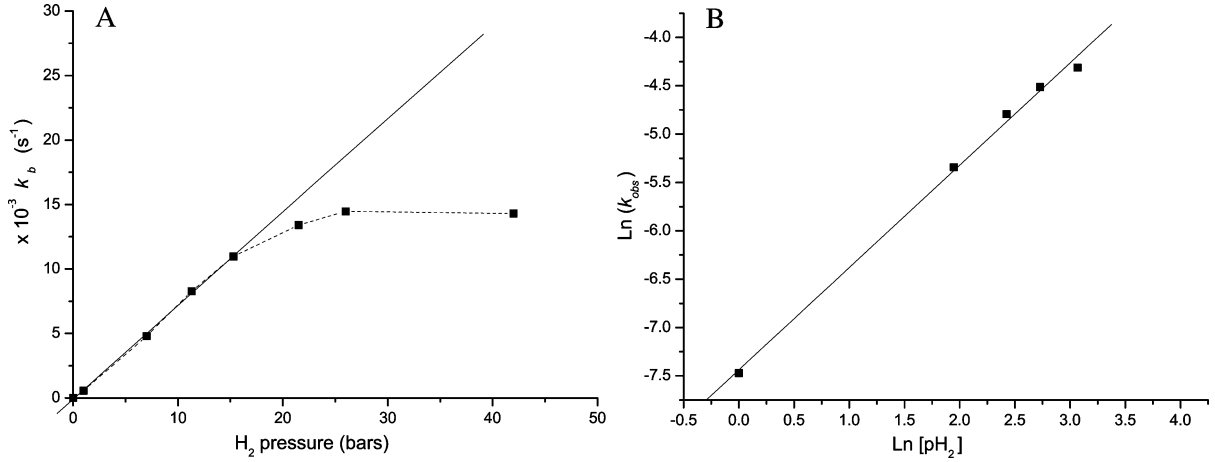


Figure 1. (A) Plot of the rate of hydrogenation versus the dihydrogen pressure. (B) Plot of $\ln(k_{obs})$ versus $\ln(pH_2)$. Conditions as given in Table 1.

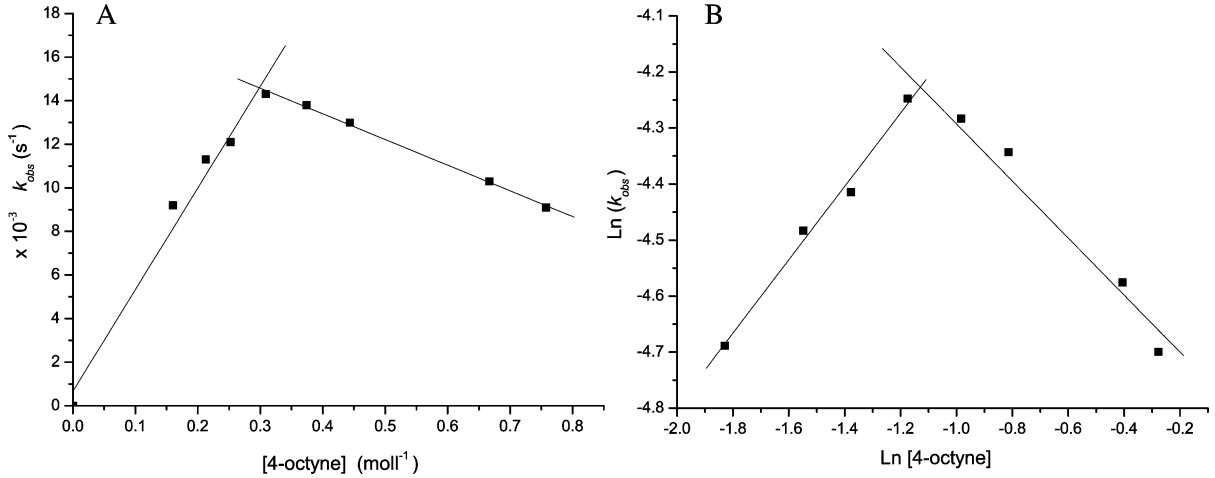


Figure 2. (A) Plot of the rate of hydrogenation versus the 4-octyne concentration. (B) Plot of ln(rate) versus ln[4-octyne]. Conditions as given in Table 2.

time. Furthermore, it appeared that the rate of 4-octyne hydrogenation employing complex **2** was about 2 orders of magnitude higher (TOF up to 18 000) than that for [Pd(Ar-bian)] complexes that contain more electron-donating ligands (e.g., *p*-MeC_6H_4-bian, *p*-$MeOC_6H_4$-bian). Finally, the use of deuterium has confirmed that molecular hydrogen (deuterium) is the source of the added hydrogen atoms in the [Pd(Ar-bian)]-catalyzed semi-hydrogenation reaction.

Dependence of the Reaction Rate on the Dihydrogen Pressure. The dihydrogen pressure was varied between 0 and 40 bar while keeping the 4-octyne and the catalyst concentrations constant at 0.31 M and 0.2 mM, respectively. Up to 15 bar of dihydrogen pressure, the reaction rate depends linearly on the dihydrogen pressure (see Figure 1A). Plots of ln(rate) versus ln $p(H_2)$ result in a straight line for dihydrogen pressures between 1 and 15 bar, yielding a slope 1.01, showing that the hydrogenation of 4-octyne is first order in dihydrogen pressure (see Figure 1B). The values of k_{obs} are listed in Table 1.

At dihydrogen pressures higher than 25 bar, the hydrogenation activity (k_{obs}) remains constant (compare entries 6, 7, and 8 of Table 1). The apparent zeroth-order dependence on the dihydrogen pressure suggests that the reaction rate is limited by the mass transfer of dihydrogen gas into the THF solution. In such a case, the dihydrogen gas concentration in solution is no longer proportional to the applied hydrogen pressure, and consequently, a zeroth-order dependency is observed. While the observed reaction rate (k_{obs}) is constant, the k_{cat} progressively decreases with increasing pressure (see Table 1). The stereoselectivity of the reaction is not affected by the hydrogen pressure, and the ratio of (*Z*)-oct-4-ene/(*E*)-oct-4-ene/octane typically remains 95/5/0.

Table 1. Kinetic Data for the Hydrogenation of 4-Octyne to 4-(*Z*)-Octene by [Pd{(*m*,*m*′-$(CF_3)_2C_6H_3$)-bian}(ma)] (**2**)[a]

entry	$p(H_2)$ (bar)	10^{-4} [Pd] (mol L^{-1})	[4-octyne] (mol L^{-1})	10^{-3} k_{obs} (s^{-1})	k_{cat} (mol^{-2} L^2 bar^{-1} s^{-1})	selectivity *Z*/*E*/alkane[b]
1	0	1.0	0.31	0	0	
2	1.0	1.0	0.31	0.6	18	94/6/0
3	7.0	1.0	0.31	4.7	22	95/5/0
4	11.3	1.0	0.31	8.3	24	93/7/0
5	15.3	1.0	0.31	11.0	23	95/5/0
6	21.5	1.0	0.31	13.4	20	95/5/0
7	26.0	1.0	0.31	14.4	18	94/6/0
8	40.0	1.0	0.31	14.3	12	93/7/0

[a] Conditions: reactions were carried out in a stainless steel autoclave. Stirring speed was set at 1250 rpm, and reaction temperature was 21 °C. [b] Selectivity determined between 10 and 90% alkyne conversion.

Dependence of the Reaction Rate on the Substrate Concentration. The substrate concentration was varied between 0.16 and 0.76 M, keeping a constant hydrogen pressure of 7 bar and the catalyst concentration at 0.2 mM. In Figure 2A, the reaction rate is plotted as a function of substrate, and it clearly shows that reaction rate reaches a maximum at a substrate concentration of 0.32 M. At lower concentrations (entries 1−5

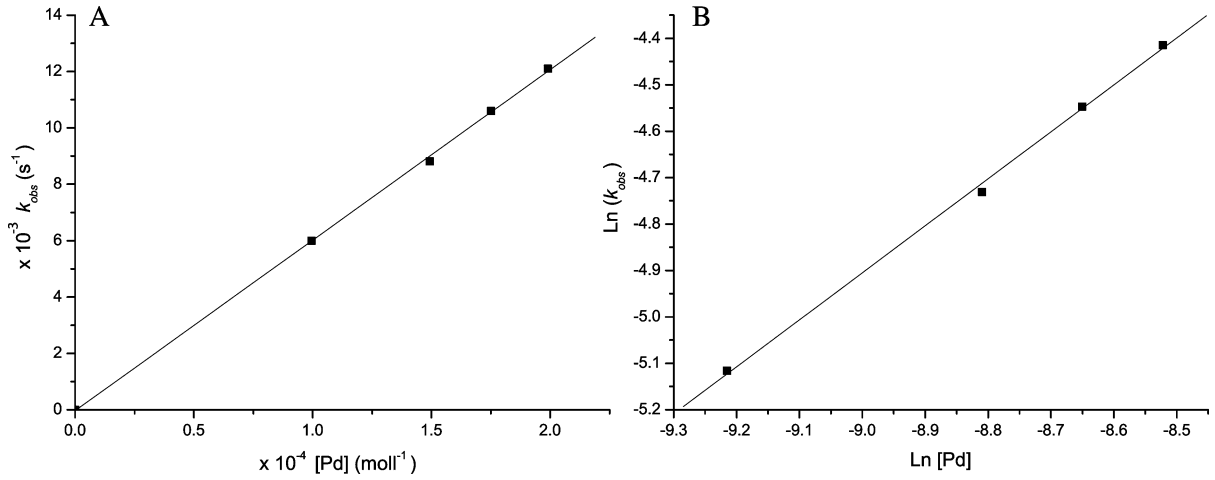


Figure 3. (A) Plot of the rate of hydrogenation versus the catalyst concentration. (B) Plot of ln(rate) versus ln[Pd]. Conditions as given in Table 4.

Table 2. Kinetic Data for the Hydrogenation of 4-Octyne to 4-(*Z*)-Octene by [Pd{(*m*,*m*′-$(CF_3)_2C_6H_3$)-bian}(ma)] (**2**)[a]

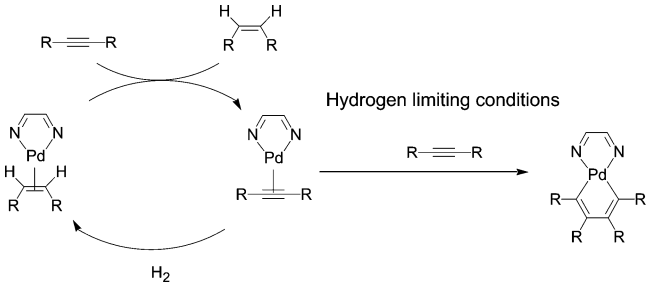
entry	p(H_2) (bar)	10^{-4} [Pd] (mol L^{-1})	[4-octyne] (mol L^{-1})	10^{-3} k_{obs} (s^{-1})	k_{cat} (mol^{-2} L^2 bar^{-1} s^{-1})	selectivity *Z*/*E*/alkane[b]
1	7.0	2.0	0	0	0	
2	7.0	2.0	0.16	9.2	41	94/6/0
3	7.0	2.0	0.21	11.3	38	95/5/0
4	7.0	2.0	0.25	12.1	35	95/5//0
5	7.0	2.0	0.31	14.3	33	95/5/0
6	7.0	2.0	0.37	13.8	27	94/6/0
7	7.0	2.0	0.44	13.0	21	95/5/0
8	7.0	2.0	0.67	10.3	11	95/5/0
9	7.0	2.0	0.76	9.1	8.6	95/5/0

[a] Conditions: reactions were carried out in a stainless steel autoclave. Stirring speed was set at 1250 rpm, and reaction temperature was 21 °C. [b] Selectivity determined between 10 and 90% alkyne conversion by GC.

in Table 2), ln(rate) versus ln([substrate]) gives a straight line with a slope of 0.65 (see Figure 2B). The positive broken reaction order suggests that the substrate is involved in a pre-equilibrium that precedes the rate-determining step.

At concentrations higher than 0.32 M, the order in substrate changes from +0.65 to −0.50, and 4-octyne becomes an inhibitor for the hydrogenation reaction. The negative order of −0.50 suggests that two substrate molecules are involved in the inhibition (rate dependence of 1/[4-octyne]^2). This change is caused by the rate-limiting dissolution of dihydrogen gas in combination with the high alkyne concentration. Inspecting Tables 1 and 2 (compare entry 8 with entry 5, respectively) shows indeed that the rates of the hydrogenation reaction (expressed in k_{obs}) are identical. At this rate, the mass transfer requirements of dihydrogen into the THF solution cannot be met, and the incipient [Pd(Ar-bian)(alkyne)] complex exists long enough to react with a second substrate molecule to form a palladacycle (see Scheme 2). The latter is, in turn, inactive under these reaction conditions, thereby reducing the amount of active hydrogenation catalyst and, hence, the overall observed catalytic activity. It has been described by Mosely et al.[18] and by Ito et al.[19] that stronger σ-donating ligands (e.g., N-donor ligands) favor the formation of the palladacyclopentadiene instead of the [Pd^0(η^2-alkyne)] complex.

Scheme 2. Formation of a Palladacycle



Attempts to isolate this palladacycle failed due to the instability of this compound, which is in accordance with reports from other authors who were unable to prepare or isolate a palladacycle arising from 4-octyne.[20,21] The absence of hexa-(*n*-propyl)benzene in the reaction mixture formed by the trimerization of 4-octyne suggests that the palladacycle is inactive and acts as a sink of catalyst species (catalyst deactivation product).

Dependence of the Reaction Rate on the Catalyst Concentration. The catalyst concentration was varied between 0 and 0.25 mM, keeping the dihydrogen pressure constant at 7 bar and 4-octyne concentration at 0.31 M. The reaction rate shows a linear dependency with respect to the palladium concentration (see Figure 3A). Plotting ln(rate) versus ln[Pd], as presented in Figure 3B, yields a straight line of slope 1.08, showing that the hydrogenation of 4-octyne is first order in palladium. The values of k_{obs} are listed in Table 3. At concentrations higher than 2.0×10^{-4} mol L^{-1}, the activity decreased; unfortunately, we were not able to determine the order in palladium at high catalyst concentrations due to the poor reproducibility of the reaction in this concentration domain. This suggests that the precatalyst is not completely activated during the induction period. In addition, at the higher reaction rates, the required rate of dihydrogen consumption cannot be met, which again results in the formation of inactive palladacycles.

Derivation of the Experimental Rate Law. The results presented here lead us to formulate the overall experimental rate law for the stereoselective hydrogenation of 4-octyne

(18) Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1971**, 1604−1605.
(19) Ito, T.; Hasegawa, S.; Takahashi, Y.; Ishii, Y. *J. Chem. Soc., Chem. Commun.* **1972**, 629−630.
(20) van Belzen, R.; Klein, R. A.; Kooijman, H.; Veldman, N.; Spek, A. L.; Elsevier, C. J. *Organometallics* **1998**, *17*, 1812−1825.
(21) van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L. *Inorg. Chem.* **1994**, *33*, 1521−1531.

Table 3. Kinetic Data for the Hydrogenation of 4-Octyne to (*Z*)-Oct-4-ene by [Pd{(*m*,*m*′-$(CF_3)_2C_6H_3$)-bian}(ma)] (**2**)[a]

entry	p(H_2) (bar)	10^{-4} [Pd] (mol L^{-1})	[4-octyne] (mol L^{-1})	10^{-3} k_{obs} (s^{-1})	k_{cat} (mol^{-2} L^2 bar^{-1} s^{-1})	selectivity *Z*/*E*/alkane[b]
1	7.0	0	0.31	0	0	
2	7.0	1.0	0.31	6.0	28	95/5/0
3	7.0	1.5	0.31	8.8	27	95/5/0
4	7.0	1.75	0.31	10.6	28	94/6/0
5	7.0	2.0	0.31	12.1	28	95/5/0

[a] Conditions: reactions were carried out in a stainless steel autoclave. Stirring speed was set at 1250 rpm, and reaction temperature was 21 °C. [b] Selectivity determined between 10 and 90% alkyne conversion by GC.

Table 4. Kinetic Data for the Hydrogenation of 4-Octyne to 4-(*Z*)-Octene by [Pd{(*m*,*m*′-$(CF_3)_2C_6H_3$)-bian}(ma)] (**2**) at Different Temperatures[a]

entry	*T* (°C)	10^{-3} k_{obs} (s^{-1})	selectivity *Z*/*E*/alkane[b]
1	21.0	14.0	95/5/0
2	25.4	15.3	95/5/0
3	29.0	20.5	95/5/0
4	36.5	25.9	94/6/0

[a] Conditions: reactions were carried out in a stainless steel autoclave; [4-octyne] = 0.31 M, [**2**] = 2.0 mM, and H_2 pressure = 7.0 bar. Stirring speed was set at 1250 rpm. [b] Selectivity determined between 10 and 90% alkyne conversion by GC.

catalyzed by **2** in THF (under conditions where dihydrogen is nonlimiting) as follows (see Supporting Information, S1):

$$\frac{-\mathrm{d}[\text{4-octyne}]}{\mathrm{d}t} = k[\text{4-octyne}]^{0.65}[\mathrm{Pd}]p\mathrm{H}_2 \qquad (1)$$

Equation 1 shows the first order in palladium catalyst and dihydrogen pressure and the broken order of 0.65 for 4-octyne. However, under hydrogen-limiting reaction conditions (e.g., high substrate or catalyst concentrations), the kinetics and, hence, the rate law change and eq 1 is no longer applicable. The selectivity observed for the hydrogenation reaction is typically 95/5/0 ((*Z*)-oct-4-ene/(*E*)-oct-4-ene/octane) and appears to be independent of the reaction conditions (see Tables 1−3). The constant stereoselectivity of the 4-octyne hydrogenation under all conditions (both dihydrogen-rich and dihydrogen-limiting reaction conditions) suggests that a single mechanism is operative.

Temperature Dependence of the Reaction Rate and Activation Parameters. The effect of temperature on the hydrogenation rate was studied in the range 20−36 °C, at a 4-octyne concentration of 0.31 M, a catalyst concentration of 2.0 mM, and a dihydrogen pressure of 7.0 bar. The Eyring plot constructed from the obtained kinetic data is shown in Figure 4 yielding the following activation parameters; $\Delta H^{\ddagger} = 30 \pm 2$ kJ mol^{-1}; $\Delta S^{\ddagger} = -180 \pm 14$ J K^{-1}. Similar values have been reported for ruthenium- and nickel-catalyzed hydrogenation of alkenes.[22,23] The large negative value for the entropy of activation ($\Delta S^{\ddagger}$) indicates a highly ordered transition state commensurate with the interaction of a dihydrogen molecule with the palladium center.

Reactions Involving the Platinum Model Catalyst [Pt{(*m*,*m*′-$(CF_3)_2C_6H_3$)-bian}(ma)] (3). Metal complexes of the

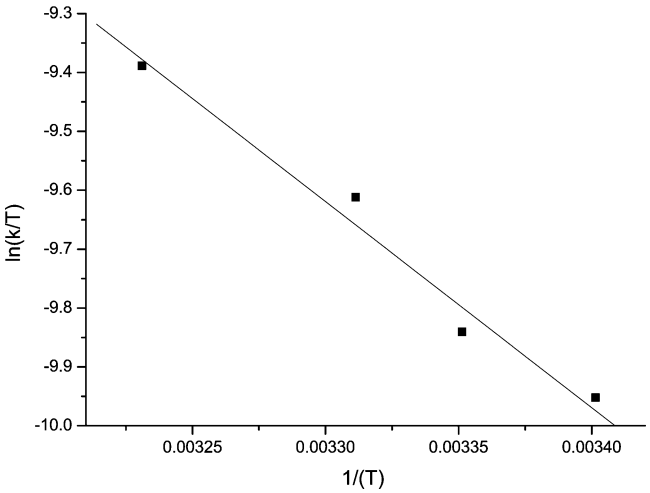


Figure 4. Eyring plot of the stereoselective hydrogenation of 4-octyne by **2**.

5*d* series typically form stronger bonds with ligands (for example to carbon) than their 3*d* and 4*d* counterparts.[1,24] These third-row transition metal complexes are generally less active in catalytic reactions and, hence, can serve as stable models of reactive intermediates proposed for a catalytic transformation. Due to the fast kinetics of **2** in the semi-hydrogenation reaction of 4-octyne, intermediates could neither be identified nor detected by standard or PHIP NMR techniques (vide infra). Therefore, recourse was taken to the platinum analogue [Pt{(*m*,*m*′-$(CF_3)_2C_6H_3$)-bian}(ma)] (**3**) that was synthesized by reacting [Pt(nbe)$_3$] (nbe = norbornene) with the *m*,*m*′-$(CF_3)_2C_6H_3$-bian ligand and maleic anhydride in THF.[25] Compound **3** could be isolated in 45% yield and was characterized by NMR, mass spectroscopy, and elemental analysis.

Hydrogenation reactions of 4-octyne using [Pt{(*m*,*m*′-$(CF_3)_2C_6H_3$)-bian}(ma)] (**3**) as the catalyst (ratio 4-octyne/**3** = 100) in acetone-d_6 at 21 °C were followed by ^{1}H NMR. In the ^{1}H NMR spectrum, only broad aromatic signals were detected, and no distinct platinum complexes could be identified. When the reaction was performed under dihydrogen-limiting conditions (2 mmol of dihydrogen, 0.013 mmol catalyst, and a ratio substrate/catalyst of 300 at 60 °C in THF), the color of the solution changed from dark purple to dark red, indicating that a new platinum species was formed. This new air- and moisture-stable platinum complex could be isolated and characterized by NMR, IR, and mass spectroscopy. From these spectroscopic data, it was concluded that the obtained red solid was [{(*m*,*m*′-$(CF_3)_2C_6H_3$)-bian}platina-2,3,4,5-tetra(propyl)cyclopentadiene] (**4**), which had been formed by an oxidative coupling (see Scheme 3). Such platinacyclopentadienes have been reported in the literature as an intermediate in the cyclotrimerization, isomerization, and polymerization of alkynes and have so far only been isolated for alkynes bearing more electron-withdrawing groups (e.g., alkoxycarbonyl or phenyl moieties).[18,26] The ease of formation of the [{(*m*,*m*′-$(CF_3)_2C_6H_3$)-bian}platina-2,3,4,5-tetra(propyl)cyclopentadiene] (**4**) under dihydrogen-limiting conditions suggests that, during the hydro-

(22) Huh, S.; Cho, Y.; Jun, M.-J. *Polyhedron* **1994**, *13*, 1887−1894.
(23) Angulo, I. M.; Lok, S. M.; Quiroga Norambuena, V. F.; Lutz, M.; Spek, A. L.; Bouwman, E. *J. Mol. Catal. A* **2002**, *187*, 55−67.
(24) Tolman, C. A.; Faller, J. W. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; pp 13−109.
(25) Sprengers, J. W.; De Greef, M.; Duin, M. A.; Elsevier, C. J. *Eur. J. Inorg. Chem.* **2003**, 3811−3819.

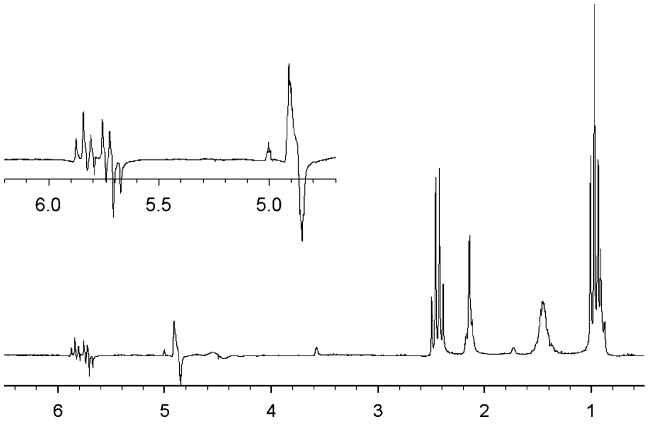
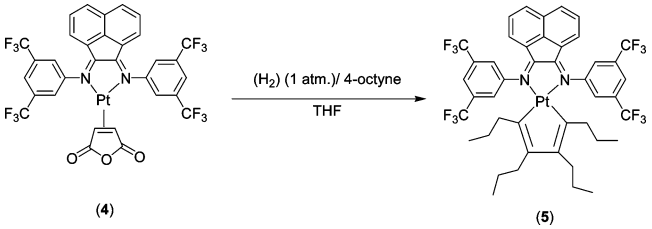


Figure 5. PHIP signals in the hydrogenation of 1-hexyne to 1-hexene with complex (**2**) (d1 = 10 s). Substrate, 1-hexyne (100 mL); solvent, acetone-d_6 (1200 mL), amount catalyst = 2 mg, temperature = 29 °C.

Scheme 3. Formation of the Platinacyclopentadiene (**5**) by Oxidative Coupling of Two Alkyne Moieties



genation experiments using **2**, a similar palladacycle may be formed, albeit probably in low concentrations.

PHIP NMR Studies. To ensure that the symmetry breaks down during the catalytic hydrogenation, the PHIP experiments presented in this paper have been carried out using the asymmetric substrates 1-hexyne and phenyl acetylene.[27] The reactions were conducted at 29 °C in THF-d_8 using [Pd{(*m*,*m*′-$(CF_3)_2C_6H_3$)-bian}(ma)] (**2**) as catalyst. Under these conditions, polarization signals were observed in the product (*Z*)-alkene upon hydrogenating 1-hexyne as well as phenyl acetylene with dihydrogen samples that were enriched in parahydrogen (see Figure 5). This demonstrates that the palladium-catalyzed hydrogenation reaction proceeds by an overall pairwise addition of the two hydrogen atoms from H_2 to the substrate and may involve a palladium(alkyne)−hydride species (such as **B** in Scheme 4). Since the polarized signals are only observed in the hydrogenation product, the exact nature of these palladium−hydride species is not revealed within the PHIP NMR experiments. Therefore, the proposed palladium−hydride species can then arise by either homolytic (i.e., oxidative addition) or heterolytic activation. (vide infra). The latter pathway has recently been established by theoretical calculations of a palladium-catalyzed semi-hydrogenation reaction as a feasible route for *cis*-product formation, whereas the oxidative addition pathway yielded only less likely, high-energy pathways.[28a]

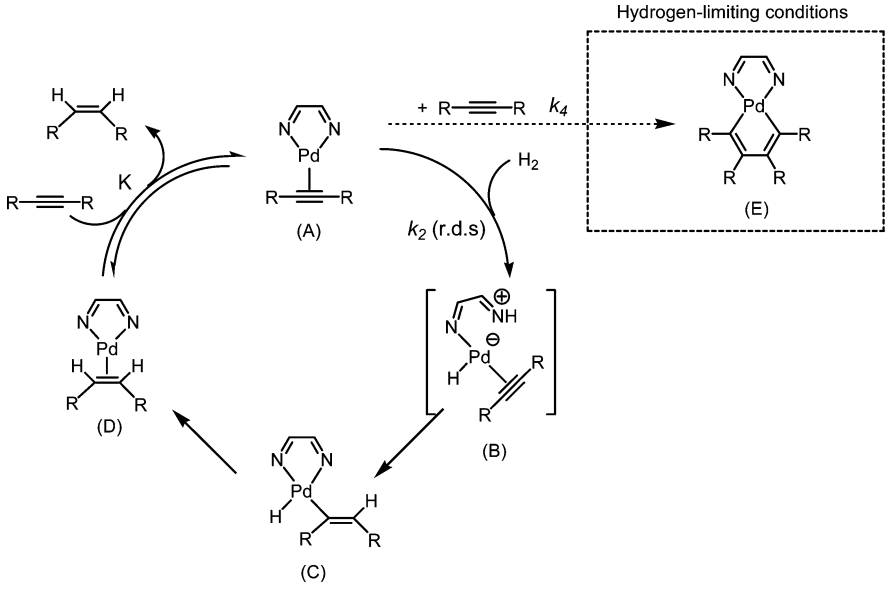
It should be emphasized, that polarization signals were *not* detected in the (*E*)-alkene, which was produced in minor amounts (5%) during the hydrogenation. This is clear evidence for the fact that the (*E*)-alkene does *not* arise from direct hydrogenation of the alkyne (vide infra).

Attempts to detect palladium−hydride species failed due to the short lifetime of the reactive intermediates, and hence, polarization signals were only observed of the hydrogenated product (i.e., the (*Z*)-alkene). Even when the substrate was omitted to avoid depletion of palladium−hydride species by a fast hydrogenation reaction, no polarization signals were detected, and the catalyst rapidly decomposed to palladium metal.

In addition, attempts were made to detect signals produced by the hydrogenation of the proposed palladacycle (**E**, Scheme 4) that is formed under dihydrogen-limiting conditions. To ensure that the palladacycle was formed during the hydrogenation reactions, an asymmetric substrate, the 3-phenyl propynoic acid ethyl ester, was chosen because it is known to easily form palladacycles.[29] Furthermore, the time between parahydrogen bursts was extended (up to 30 min) to allow the reaction to occur between the palladium catalyst and the substrate. Although *cis*-hydrogenation of the alkyne to (*Z*)-alkene was still observed, neither polarization signals nor normal signals were detected arising from the palladacycle.

It must to be noted that the observed polarization signals for hydrogenation products catalyzed by complex **2** in nonprotic

Scheme 4. Catalytic Cycle of the Stereoselective Semi-Hydrogenation of 4-Octyne



solvents were only 1 order of magnitude higher than the thermal signals produced in a normal NMR. While the enhancement of the ^{1}H NMR sensitivity by PHIP can theoretically reach values of 10^4-10^5, it typically ranges about a factor of 10^3-10^4.[30] The small enhancement of the polarization in this case is explained by the type of dihydrogen activation, that is, the heterolytic dihydrogen activation across one of the Pd−N bonds. This would lead to a large chemical-shift difference in the proposed zwitterionic intermediate (**B**; Scheme 4), and hence, the spin correlation is rapidly lost. In addition, the large nuclear quadrupole moment of palladium (0.660×10^{-24} cm^2) can further decrease the signal intensity of the polarization signals. Hence, the proposed mechanism presented in Scheme 4 is in agreement with the findings of the parahydrogen hydrogenation experiments as well as the results of the DFT calculations.[28a] That is, the heterolytic dihydrogen cleavage coincides with the rate-limiting step (i.e., the step with the highest activation energy), and no stable intermediates are formed after the initial dihydrogen activation. To readily observe the PHIP signal at all, the reaction must be fast in an absolute sense with respect to relaxation and loss of coherence.

Mechanism for the Stereoselective Hydrogenation of 4-Octyne by [Pd{(*m*,*m*′-(CF$_3$)$_2$C$_6$H$_3$)-bian}(ma)] (2). The kinetic and spectroscopic analysis presented above enables us to propose a plausible catalytic cycle for palladium-catalyzed semi-hydrogenation of 4-octyne by complex **2**. The proposed catalytic cycle, as depicted in Scheme 4, roughly resembles the catalytic cycle proposed by van Laren et al.[12a] To enter the cycle, the coordinated maleic anhydride of the precursor catalyst is substituted (vide infra) to form the zerovalent Pd(NN)(alkyne) species (**A**), which is an active intermediate entering the catalytic cycle. It is assumed that the concentration of precursor catalyst **2** is negligible after the induction period during which species **A** is formed. This is confirmed by the zero intercept of the rate-versus-[Pd] plot and the first-order dependency of the hydrogenation rate on the palladium concentration (see Figure 3). At palladium concentrations below 0.2 mM, the amount of palladium in the catalytic cycle is thus equal to the total amount of palladium in the reaction mixture.

Under dihydrogen-rich conditions, the formation of **A** is ensued by the heterolytic dihydrogen activation to obtain the {[Pd(alkyne)(H)]$^-$(N∩NH)$^+$} species (**B**). According to high-level DFT calculations, using an extended basis set, these species easily collapse to [Pd(NN)(H)(alkenyl)] (**C**) via low-barrier processes.[28a] As mentioned in the previous paragraph, attempts to detect the palladium−hydride species (**B** or **C**) failed using PHIP NMR and catalyst **2** in the hydrogenation reaction of 1-hexyne and phenyl acetylene.

Reductive elimination of intermediate **C** yields the Pd(NN)-(alkene) species **D**. Again, the hydrogen atoms are transferred in such a way that the spin information in PHIP experiments is maintained in the primary reaction product (i.e., the (*Z*)-alkene). In principle, this can be achieved either by transferring the two hydrogen atoms in a concerted pairwise manner or by transferring them very rapidly (compared to the nuclear spin coupling constant and the spin relaxation) to the substrate in an asynchronous way. As mentioned before, this latter route is in accordance with the heterolytic dihydrogen splitting across one of the Pd−N bonds.

The broken reaction order in substrate (0.65) is explained by a pre-equilibrium between species **D** and **A** (vide infra).[28b] In the case that the dihydrogen concentration becomes limiting, or dihydrogen is no longer present during the reaction, the palladium(alkyne) complex **A** reacts with a second alkyne molecule to form the palladacycle **E**, which is an inactive palladium species.

On the basis of this hydrogenation mechanism (i.e., dihydrogen activation is the rate-determining step), the following rate expression can be derived (see Supporting Information): $r = k_{cat}[\text{octyne}][\text{Pd}]_{cat}pH_2$ with $k_{cat} = k_2k_3K_1/(k_3\{[\text{octene}] + K_1[\text{octyne}]\}$. This expression is in agreement with the experimentally derived rate law (eq 1).

Activation of the Precatalyst. The hydrogenation experiments of 4-octyne to (*Z*)-oct-4-ene were carried out using the preformed catalyst [Pd{(*m*,*m*′-(CF$_3$)$_2$C$_6$H$_3$)-bian}(ma)] (**2**). In such a case, where the coordinated alkene of the precatalyst is not identical to the substrate, the route into the catalytic cycle needs to be considered, especially since it can influence the performance of the catalyst.[29]

To enter the catalytic cycle, two possibilities that determine the faith of the coordinated maleic anhydride are envisaged: (1) the maleic anhydride is hydrogenated to succinic anhydride, or (2) the maleic anhydride is substituted by the large excess of alkyne present, and free maleic anhydride is present is solution. To investigate the latter possibility, 11 mg of [Pd{(*m*,*m*′-(CF$_3$)$_2$C$_6$H$_3$)-bian}(ma)] (**2**) was dissolved in 1 mL of acetone-d_6, and 20 μL of 4-octyne was added (Pd/alkyne ratio = 1:13). The reaction was followed with ^{1}H NMR for 90 min at 21 and 55 °C. Within this period of time, neither free maleic anhydride nor any shift of the maleic anhydride protons' resonances was observed upon the addition of 4-octyne. This implies that there is no significant exchange reaction between the coordinated maleic anhydride and the dissolved 4-octyne, confirming that electron-poor alkenes (larger π-accepting properties) coordinate more strongly to the zerovalent palladium complexes.[21]

If the maleic anhydride is hydrogenated off during the hydrogenation experiment, the reaction mixture should contain succinic anhydride. Indeed, the formation of 3,4-dideutero succinic anhydride (2.48 ppm) was detected in ^{2}H NMR spectra that were recorded when deuterium was used in the hydrogenation reaction. In a separate hydrogenation experiment (using 1 bar dihydrogen gas), the buildup of succinic anhydride was monitored by GC analysis, and the results are presented in Figure 6A.

The amount of succinic anhydride increases during the first 4 min, after which its concentration remains constant. Thus, the slow formation of the active palladium catalyst reflects the

(26) (a) Müller, C.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **2002**, *21*, 1118−1123. (b) Stephan, C.; Munz, C.; tom Dieck, H. *J. Organomet. Chem.* **1994**, *468*, 273−278. (c) tom Dieck, H.; Munz, C.; Mueller, C. *J. Organomet. Chem.* **1990**, *384*, 243−255. (d) Jones, N. L.; Ibers, J. A. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; pp 111−135. (e) Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1974**, 169−175.
(27) Haake, M.; Natterer, J.; Bargon, J. *J. Am. Chem. Soc.* **1996**, *118*, 8688−8691.
(28) (a) Dedieu, A.; Humbel, S.; Elsevier, C. J.; Grauffel, C. *Theor. Chem. Acc.* **2004**, *112*, 305−312. (b) One of the reviewers suggested a mechanism in which the alkene eliminates from a hydridopalladium(II)−vinyl complex, which may, in the presence of excess 4-octyne, form a hydridopalladium-(II)−vinyl(alkyne) complex reversibly. Hence, the formation of the hydridopalladium(II) complex would clearly depend on the alkyne concentration, but the second step would act to inhibit the reaction.
(29) van Belzen, R.; Hoffmann, H.; Elsevier, C. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1743−1745.
(30) Jang, M.; Duckett, S. B.; Eisenberg, R. *Organometallics* **1996**, *15*, 2863−2865.

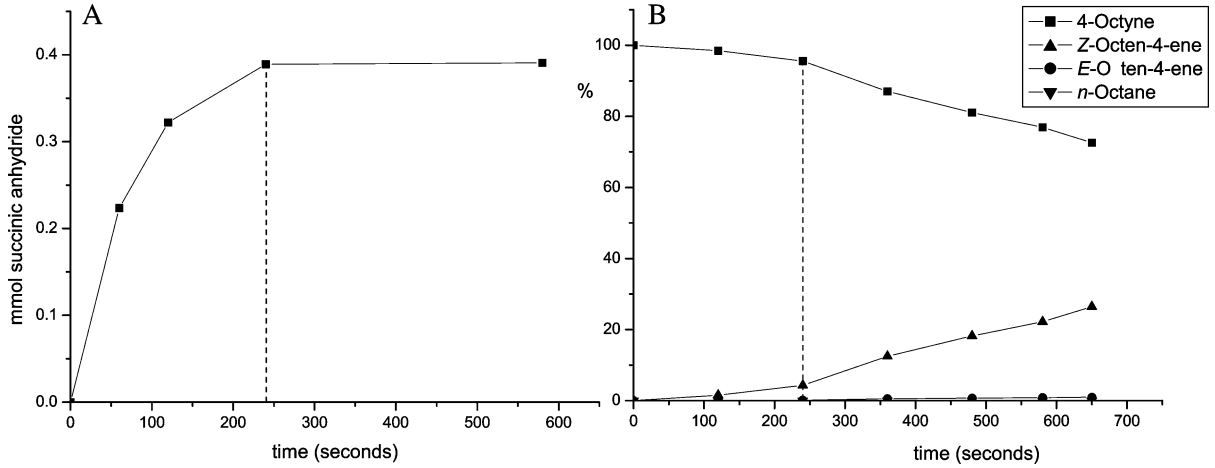
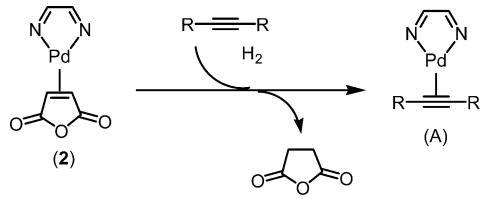


Figure 6. (A) Formation of succinic anhydride during the hydrogenation of 4-octyne. (B) Reaction profile of the hydrogenation of 4-octyne by complex **1**.

Scheme 5. Entering the Catalytic Hydrogenation Cycle



sluggish hydrogenation of maleic anhydride by [Pd(Ar-bian)-(alkene)] systems, which has also been reported by van Asselt et al.[32] The reaction profile for this hydrogenation reaction (see Figure 6B) displays a distinctive induction period (first 4 min) and coincides with buildup of succinic anhydride, showing that the coordinated maleic anhydride is gradually hydrogenated during this period, with progressive hydrogenation of 4-octyne by the palladium catalyst (see Scheme 5).

Stereoselectivity of the Hydrogenation and (*Z*)−(*E*) Isomerization. Variation of the reaction conditions (dihydrogen pressure, substrate or catalyst concentrations) does not affect the stereoselectivity of the hydrogenation reaction (see Tables 1−3), and a product distribution of 95/5/0 ((*Z*)-oct-4-ene/(*E*)-oct-4-ene/octane) is typically obtained. The high stereoselectivity, seemingly independent of the reaction conditions or conversion, merits further investigation. The formation of the (*E*)-isomer was studied using deuterium gas with both 1-octyne and phenyl acetylene as model substrate.

When complex **2** is employed as the catalyst in the hydrogenation of 1-octyne and phenyl acetylene using deuterium, there are, besides the expected deuterium signals from the *cis*-hydrogenation, also deuterium signals arising from the D^3 in the vicinal *trans* position relative to D^1 (see Figure 7). The deuteration of the D^3 position is the result of an isomerization reaction (vide infra). A similar deuteration pattern is obtained when a mixture of 1-octene and 4-octyne (ratio 1:1) is hydrogenated using deuterium (see Figure 8). In this case, the two geminal deuterium signals of 1-octene, with roughly the same intensity around 5.0 ppm, show that deuterium is incorporated in both *cis*- and *trans*-vicinal positions relative to D^1 without apparent preference (compare Figure 7B and Figure 8). This shows that 1-octene can easily compete with 4-octyne

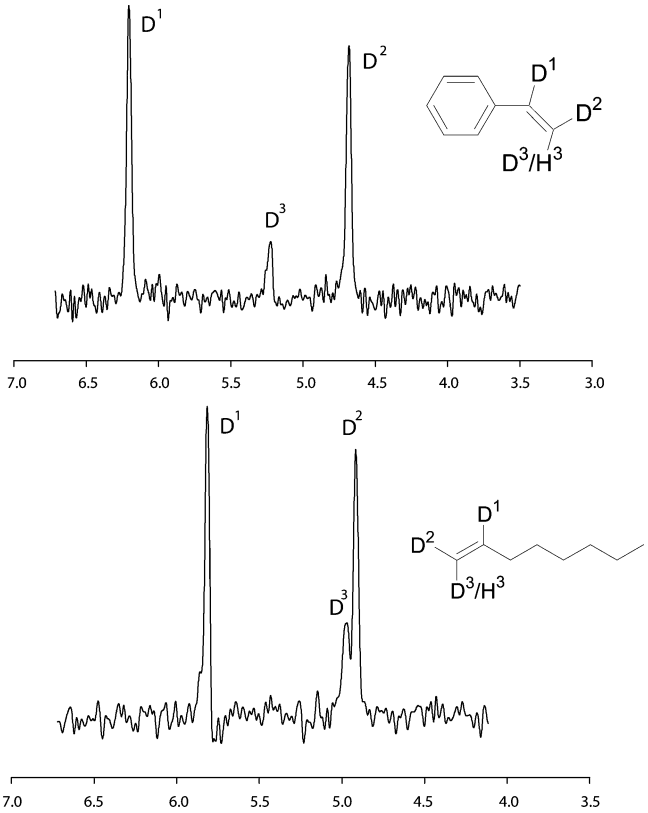


Figure 7. The 76 MHz ^{2}H NMR spectra from (a) deuteration of phenyl acetylene, and (b) deuteration of 1-octyne. Signal D^3 in spectrum proves the incorporation of the deuterium in the geminal position.

for the palladium catalyst and, while being coordinated to the palladium, be involved in an isomerization reaction.

An isomerization mechanism that operates under dihydrogen atmosphere has been independently proposed by Bargon et al. and Spencer et al. and has recently been confirmed by Duckett et al.[33] This mechanism proceeds via an equilibrium between a palladium(dihydrido)(substrate) complex and the monohydrido alkyl complex (see Scheme 6).

To gain more insight into the formation of (*E*)-oct-4-ene, the products of the hydrogenation reaction (using D_2) of the mixture

(31) Drexler, H. J.; Baumann, W.; Spannenberg, A.; Fischer, C.; Heller, D. *J. Organomet. Chem.* **2001**, *621*, 89−102.
(32) van Asselt, R.; Elsevier, C. J. *J. Mol. Catal. A* **1991**, *65*, L13−L19.
(33) (a) Dunne, J. P.; Aiken, S.; Duckett, S. B.; Konya, D.; Almeida Leñero, K. Q.; Drent, E. *J. Am. Chem. Soc.* **2004**, *126*, 16708−16709. (b) Yu, J.; Spencer, J. *J. Am. Chem. Soc.* **1997**, *119*, 5257−5258. (c) Harthun, A.; Giernoth, R.; Elsevier, C. J.; Bargon, J. *Chem. Commun.* **1996**, *21*, 2483−2484.

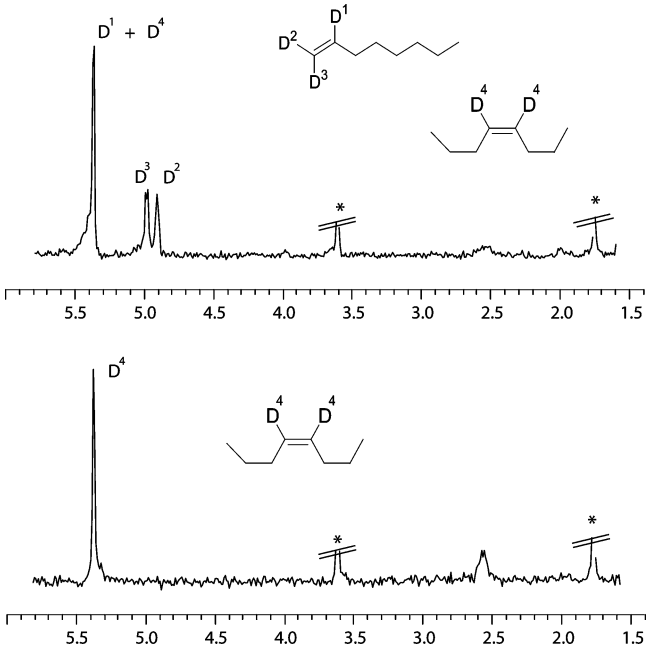


Figure 8. The 76 MHz ^{2}H NMR spectra from (a) deuteration of a mixture of 4-octyne and 1-octene, and (b) deuteration of 4-octyne. Natural abundance of deuterium in the solvent THF is marked with asterisks.

of 4-octyne ($m/z = 110$) and 4,5-$(H)_2$ (*Z*)-oct-4-ene ($m/z = 112$) (ratio 5:1) was studied by GCMS. Analysis of the (*E*)-oct-4-ene peak shows an increasing amount of 4,5-(H,D) (*E*)-oct-4-ene ($m/z = 113$). However, appropriate control experiments were required for the validation of this interpretation since the mass 113 is "contaminated" by two contributions, namely, (1) the isotope peak $[m + 1]^+$ from 4,5-$(H)_2$ (*E*)-oct-4-ene (with *m*/*z* 113, 9%) and (2) fragmentation $[m - 1]^+$ of the 4,5-$(D)_2$ (*E*)-oct-4-ene ($m/z = 114$). After correction of the latter contribution (8.8% based on *m*/*z* 114), the amount of deuterium incorporation can be expressed as a ratio of *m*/*z* 113/112 and is given in Figure 9. From this, it is concluded that a significant amount of monodeuterated (*E*)-octene is formed. This compound can *only* be formed by isomerization of the 5-$(H)_2$ (*Z*)-oct-4-ene ($m/z = 112$) present at the start of the reaction and mediated by the mechanism presented in Scheme 6.

Addition of a deuteron donor $(Et_3ND)^+(CF_3SO_3)^-$ to the reaction mixture (using 4-octyne and H_2) shows no incorporation of deuterium, and accordingly, no 4-hydro-5-deutero (*E*)-oct-4-ene ($m/z = 113$) is detected in the reaction mixture. This confirms that the reaction proceeds by incorporation of both hydrogen atoms from one molecule of dihydrogen via a palladium species that incorporates the substrate and these two

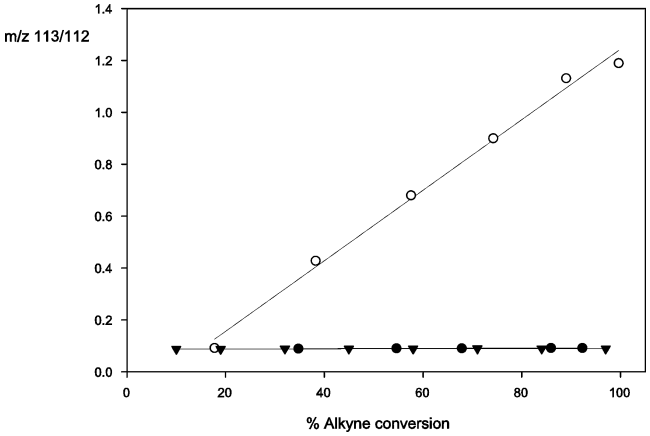


Figure 9. Plot of $m/z = 113/112$ versus alkyne conversion. Filled squares are the hydrogenation of 4-octyne with H_2. Open dots: hydrogenation of a mixture of 4-octyne and (*Z*)-oct-4-ene. Filled dots: the hydrogenation of 4-octyne with H_2 in the presence of $(Et_3ND)^+(CF_3SO_3)^-$.

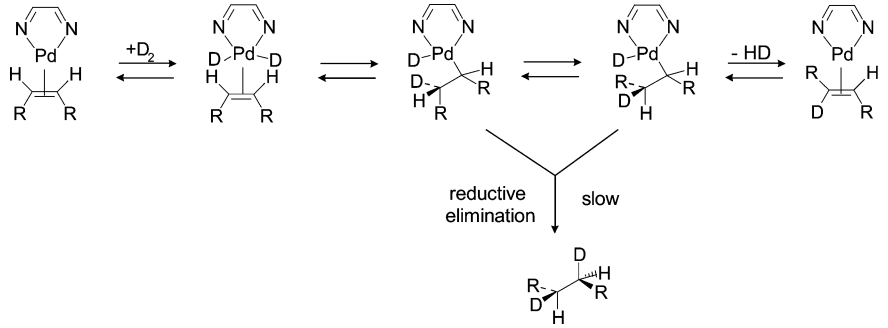
hydrogen atoms after dihydrogen cleavage. In conclusion, the primary product of the hydrogenation reaction is the (*Z*)-alkene, which may be isomerized to the (*E*)-alkene by the palladium catalyst assisted by dihydrogen gas according to a mechanism, as depicted in Scheme 6. These results are in agreement with the PHIP NMR results (vide supra).

The absence of *n*-octane in the reaction mixture suggests that the hydrogen-assisted isomerization reaction does not result in over-reduction, although a palladium(hydrido)(alkyl) species is assumed during the isomerization process. Apparently, the β-elimination, which is, in the case of palladium, known to be a very low-barrier process,[34] is much faster than the reductive elimination of the alkane from the incipient Pd(H)(alkyl) species.

Conclusions

In summary, the experimentally derived rate law for the highly stereoselective [Pd(Ar-bian)]-catalyzed hydrogenation of 4-octyne is in agreement with the proposed mechanism. The first-order dependence in palladium concentration shows that only mononuclear species are involved in the product formation. The inverse dependence of the hydrogenation activity on the substrate concentration provides evidence that an inactive palladacycle is formed under dihydrogen-limiting conditions. The high selectivity observed in the hydrogenation experiments using [Pd{(*m*,*m*′-$(CF_3)_2C_6H_3$)-bian}(ma)] complexes is explained by the relatively strong coordination of the alkyne to the palladium center, which only allows for the presence of small amounts of alkene complexes. Only the latter are responsible for the observed minor amounts of (*E*)-alkene. Since no *n*-octane

Scheme 6. Proposed Isomerization Mechanism



was detected in the reaction mixture, only a tiny amount of the intermediate Pd(hydrido)(alkyl) species will reductively eliminate to form the alkane. Thus, the combination of the stronger coordination of the alkyne and the subsequent reaction with dihydrogen results in the kinetic product, the (*Z*)-alkene.

The use of deuterium and parahydrogen gas has revealed that both hydrogen atoms of dihydrogen are transferred to the organic substrate, in an overall *cis*-pairwise manner.

Activation of the catalyst precursor **2** occurs by hydrogenation of the coordinated maleic anhydride to succinic anhydride, which accounts for the induction time and prevents the formation of palladacycles before the hydrogenation of the actual substrate starts. Substrates with more electron-withdrawing substituents, although they can be hydrogenated cleanly to the (*Z*)-isomer, readily produce palladacycles, which hamper the study of the reaction kinetics for such substrates. Finally, the overall results have enabled us to provide a viable reaction mechanism for the stereoselective hydrogenation of 4-octyne in THF by complex **2**. This new insight into the mechanism of the stereoselective semi-hydrogenation of alkynes by the complex **2** might prove to be valuable for the synthesis of organic compounds, especially those for which a high degree of (*Z*)-isomer needs to be obtained.

Experimental Section

General. Gas chromatographic analyses were run on a Varian 3300 apparatus with a DB-5 column. Dihydrogen (grade 5.0) was purchased from Air Liquide. High-pressure hydrogenation reactions were performed in a (SS 316) 50 mL stainless steel autoclave equipped with a directly fixed transmission infrared cell of IRTRAN windows (ZnS, transparent up to 700 cm^{-1}, Ø 10 mm, optical path length = 0.4 mm). The infrared option could not be used due to the low IR sensitivity of 4-octyne. The autoclave was further equipped with a magnetic mechanical stirrer near the bottom of the autoclave that provides a vigorous mixing of the solution with the gas at high speeds (max = 3400 rpm). It also provides for a fast flow through the infrared cell within several milliseconds. An electrical heater (T_{max} = 200 °C), a temperature controller, and a pressure transducing device (P_{max} = 185 bar) were also attached to the autoclave.

All syntheses of complexes and other air- and/or water-sensitive compounds were carried out and in dried glasswork, in dry solvents, using standard Schlenk techniques under an atmosphere of purified nitrogen. Diethyl ether, THF, pentane, and hexane were distilled from sodium metal; acetone was distilled from $CaSO_4$, and 1,4-dioxane and dichloromethane were distilled from CaH_2. Other chemicals were used as received. The starting materials [Pt(nbe)$_3$] and [Pd(nbd)(ma)] and the ligand (*m*,*m*′-$(CF_3)_2$ C_6H_3)-bian were prepared according to literature procedures.[17,25,35]

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 spectrometer (^{1}H, 300.13 MHz; ^{13}C, 75.48 MHz; ^{19}F, 282.41 MHz; ^{2}H, 76 MHz) or on a Varian Unity Inova 500 spectrometer (^{1}H, 499.86 MHz; ^{13}C, 125.70 MHz). Positive chemical shifts (ppm) are denoted in the ^{1}H and ^{13}C NMR spectra to higher frequency from an external tetramethylsilane reference and in the ^{19}F NMR spectra to higher frequency from an external $CFCl_3$ reference. ^{2}H NMR spectra were recorded unlocked, and the chemical shifts are denoted with respect to an internal acetone-d_6 reference.

High-resolution mass spectrometry (HRMS) measurements were carried out at Swammerdam Institute of Life Sciences (SILS), University of Amsterdam, The Netherlands. The Electron Impact (EI) and the Fast Atom Bombardment (FAB) mass spectrometry measurements were carried out using a JEOL JMS SX/SX 102A four-sector mass spectrometer, coupled to a JEOL MS-MP9021D/UPD system program. In the EI-MS measurements, the samples were introduced into the ion source via a direct insertion probe. In the FAB-MS measurements, the samples were loaded in a matrix solution (3-nitrobenzyl alcohol) on to a stainless steel probe and bombarded with xenon atoms with an energy of 3 keV. During the high-resolution EI-MS and the FAB-MS measurements, a resolving power of 10 000 (10% valley definition) was used. Low-resolution mass spectrometry (MS) measurements were performed in the EI mode (70 eV) on a GCMS HP 5890/5971 apparatus equipped with a ZB-5 column (5% cross-linked phenyl polysiloxane) with an internal diameter of 0.25 mm and film thickness of 0.25 μm.

Hydrogenation Reactions. The kinetic studies of the catalytic semi-hydrogenation of 4-octyne in THF with **2** as catalyst precursor have been performed by using the initial rates method. Under the reaction conditions used, the first 10% conversion of 4-octyne was discarded, during which the catalyst's activity increased (induction period). The rate of the reaction was measured between 10 and 90% alkyne conversion and was fitted to a straight line, yielding R^2 values higher than 0.99. For obtaining the reaction orders of the hydrogenation reaction, the dihydrogen pressure (between 0 and 40 bar), catalyst (0 and 4 mmol L^{-1}), and substrate concentrations (between 0.76 mol L^{-1}) were separately changed.

More specifically, for a given amount of dihydrogen pressure, catalyst, and substrate concentration (as given in Tables 1−3), a typical hydrogenation experiment can be described as follows: the desired amount of 4-octyne (0.5−4.5 mL) was taken from the bottle using a 1 mL (or 5 mL) plastic syringe and was then transferred to the high-pressure autoclave. The exact amount was determined by weighing the full syringe (syringe + 4-octyne) and weighing it again after it has been emptied into the autoclave. The desired amount of catalyst (0−20 μmol) was weighed in a 20 mL vial. This amount was then dissolved in 0.5 mL of THF, which was then transferred, using a syringe, to the autoclave. The vial was then washed three times with ca. 0.5 mL of THF to ensure that all of the catalyst was transferred to the autoclave. Then, 13 mL of THF was added to the autoclave (total amount of solvent is 15 mL), after which the autoclave was closed. The electronic stirrer was started (stirring rate was 1250 rpm), and the experiment was started by applying the desired amount of dihydrogen pressure (0−40 bar). During the hydrogenation reaction, small aliquots (∼1 mL) were taken at regular intervals (0.5−2 min) under constant dihydrogen pressure. The samples were analyzed by GC to determine the alkyne conversion and the selectivity toward the reaction products (i.e., (*Z*)-oct-4-ene, (*E*)-oct-4-ene, and octane). After every hydrogenation run, the autoclave was subjected to thorough cleaning and blanc reaction to ensure the autoclave was not active due to the presence of undesired metallic palladium.

The variable temperature experiments were executed by first charging the autoclave with 4-octyne and 13 mL of THF. The autoclave was closed and allowed, with stirring (1250 rpm), to reach the reaction temperature (preset temperature between 20 and 36 ± 0.2 °C). The catalyst (5.7 μmol) was dissolved in 2 mL of THF and injected with H_2 gas (7 bar) into the autoclave. Samples were taken every 30 s, which were analyzed by GC.

After every experiment, the autoclave was cleaned by rinsing it with acetone. The autoclave was then taken apart, and all of the components that were in contact with the reaction mixture were carefully cleaned with aqua regia. All components were washed successively with H_2O and twice with acetone. All metallic components were then cleaned with silver polish to remove metal chloride and metal nitrate salts. The autoclave components were washed with acetone and dried. To ensure that all palladium metal was removed, a blanc experiment was performed (15 mL of THF, 0.5 mL of 4-octyne, 30 bar H_2 omitting the catalyst). After a reaction time of 1 h (20 times the normal reaction

(34) Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109−7116.
(35) Crascall, L. E.; Spencer, J. L. *Inorg. Synth.* **1990**, *28*, 126−132.

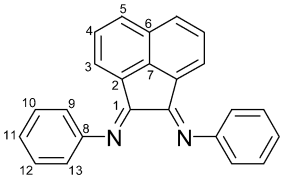


Figure 10. Numbering scheme for Ar-bian ligands.

time), the reaction mixture was analyzed by GC. When the conversion was less then 2%, the autoclave was considered clean.

Hydrogenation Reactions using Deuterium. For hydrogenation reactions using deuterium gas, a 5 mm NMR tube was filled with a 1 mL THF solution containing 1 mg of complex **2** and 30 μL of substrate. The NMR tube was gently purged with 1.1 bar of deuterium gas for 30 s, after which a NMR spectrum was taken.

In Situ Hydrogenation Using Parahydrogen. Para-enriched dihydrogen containing about 50% para-H_2 was prepared by passing H_2 through an activated charcoal reactor at 77 K at a pressure of 3 bar, as described in the literature.[34] The hydrogenations with parahydrogen were carried out in situ. For this purpose, a glass capillary connected to the parahydrogen source was lowered into the NMR probe actuated by an electromagnet (i.e., by a solenoid), which is electrically controlled by the computer console of the NMR spectrometer. In this fashion, parahydrogen can be bubbled through the reaction mixture for a defined period of time followed by the detection pulse of the NMR experiment. In most cases, a hydrogenation time of 5−10 s has turned out to be sufficient. About 2 s after the dihydrogen addition has stopped, the NMR detection was started. This procedure can be repeated to afford a subsequent accumulation of several scans, which yielded a good signal-to-noise ratio of the PHIP resonances. In addition, phase-selective accumulation of data can be used to suppress signals of components that are not involved in the hydrogenation or to separate PHIP signals from standard resonances by appropriately selecting only the two-spin order of PHIP.

Five millimeter NMR tubes were charged with 100 μL of substrate, 2 mg of catalyst **2**, and 1200 μL of deuterated solvent and placed into a 200 MHz spectrometer. *p*-H_2 enriched to 50% was prepared via catalytic equilibration over charcoal at 77 K and injected repeatedly in synchronization with the pulsed NMR experiment via an electromechanically lowered glass capillary mechanism. Higher levels of *p*-H_2 enrichment, namely, >97%, were achieved for some of the reactions using a closed cycle cooler cryostat.

Synthesis. The atomic numbering for the Ar-bian ligands is given in Figure 10.

[Pd{(*m*,*m*′-$(CF_3)_2C_6H_3$)-bian}(ma)] (2). An amount of 0.40 g (1.12 mmol) of (*m*,*m*′-$(CF_3)_2C_6H_3$)-bian was dissolved in dry THF (10 mL). Then, Pd(nbd)(ma) (0.40 g, 1.34 mmol) was added, and the reaction mixture was stirred for 20 min at room temperature. The reaction mixture was filtered through Celite filter aid under N_2 atmosphere to remove traces of metallic palladium. The Celite filter aid was repeatedly washed with dry THF (3 × 5 mL) until the washings were colorless. The combined filtrates were evaporated to dryness in vacuo, and the last traces of solvent were removed by stripping with dry pentane. Then, the product was carefully washed with dry pentane and dried in vacuo. ^{1}H NMR (499.84 MHz, acetone-d_6): δ 8.40 (d, J(H,H) = 8.5 Hz, 2H, Ar-H^5), 8.24 (br, 4H, Ar-$H^{9,13}$), 8.19 (br, 2H, Ar-H^{11}), 7.75 (pst, 2H, Ar-H^4), 7.46 (d, 2H, J(H,H) = 7.5 Hz, Ar-H^3), 4.25 (br, 2H, C═C−H). ^{13}C NMR (125.70 MHz, acetone-d_6): δ 171.11 (C═O), 1740.40 (C_1), 151.11 (C_8), 146.29 (C_7), 133.86 (q, ^2J(C,F) = 33.3 Hz, C_{10}, C_{12}), 133.11 (C_5), 132.73 (C_6), 129.90 (C_4), 127.44 (C_2), 125.86 (C_3), 124.19 (q, ^1J(C,F) = 271 Hz, Ar−CF_3), 123.27 (C_9, C_{13}), 122.22 (C_{11}), (C═C of alkene not resolved). ^{19}F NMR (282.41 MHz, acetone-d_6): δ −63.16. IR (KBr): 1840 (C═O), 1730 (C═O). Anal. Calcd for $C_{32}H_{14}F_{12}N_2O_3$-Pd: C, 47.52; H 1.74; N 3.46. Found: C, 47.65; H, 1.81; N, 3.43.

[Pt{(*m*,*m*′-$(CF_3)_2C_6H_3$)-bian}(ma)] (3). Pt(nbe)$_3$ (70.6 mg, 0.15 mmol), (*m*,*m*′-$(CF_3)_2C_6H_3$)-bian (92.8 mg, 0.15 mmol), and maleic anhydride (15.0 mg, 0.15 mmol) were dissolved in dry THF. The reaction mixture was allowed to react for 5 days at 21 °C, during which the color changed from yellowish brown to purple. The solvent was evaporated, and the residue was dissolved in 2 mL of dichloromethane. After addition of 20 mL of pentane, a purple solid deposited from solution. The solvent was removed by decanting. The products were washed with pentane (3 × 20 mL) and dried in vacuo. The yield was 55.6 mg (45%). ^{1}H NMR (300.13 MHz, acetone-d_6): δ 8.51 (d, 2H, J(H,H) = 8.7 Hz, Ar-H^5), 8.50 (br, 4H, Ar-$H^{9,13}$), 8.24 (br, 2H, Ar-H^{11}), 7.71 (d, 2H, J(H,H) = 7.5 Hz, Ar-H^4), 7.70 (pst, 2H, Ar-H^3), 3.70 (br, 2H, J(Pt,H) = 42 Hz, C═C−H). No ^{13}C was recorded due to the limited solubility and stability of the complex. ^{19}F NMR (282.41 MHz, acetone-d_6): δ −63.47. Anal. Calcd for: C, 42.82; H, 1.57; N, 3.12. Found: C, 42.67; H, 1.63; N, 3.04.

[(*m*,*m*′-$(CF_3)_2C_6H_3$)-bian]platina-2,3,4,5-tetra(propyl)cyclopentadiene (4). A sealed tube equipped with a magnetic stirring bar was charged with 0.5 mL of octyne (4.0 mmol) and 2 mL of THF. To this solution was added Pt[(*m*,*m*′-$(CF_3)_2C_6H_3$)-bian](ma) (**4**) (12.2 mg, 0.013 mmol), and the solution was purged with dihydrogen gas for 3 min. The tube was quickly sealed and heated to 60 °C for 60 min, during which the purple solution gradually turned dark red. After the reaction mixture was cooled to room temperature, the solvent was removed by purging with a gentle stream of nitrogen. After the volume was reduced to 0.5 mL, 50 mL of pentane was added, and the red complex precipitated from the solution. The solvent was removed with a cannula, and the residue was dried in vacuo. The yield was 11.5 mg (85%). ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 8.47 (d, 2H, J(H,H) = 8.1 Hz, Ar-H^5), 8.19 (s, 2H, Ar-H^{11}), 8.08 (s, 4H, Ar-$H^{9,13}$), 7.59 (pst, 2H, Ar-H^4), 7.07 (d, 2H, J(H,H) = 7.5 Hz, Ar-H^3), 3.4 (m, 4H, CH_2), 2.8 (m, 4H, CH_2), 1.3 (m, 8H, CH_2), 0.9 (t, 12H, CH_3). ^{13}C NMR (75.48 MHz, acetone-d_6): δ 148.0 (C_7), 146.3 (C_6), 132.7 (q, ^2J(C,F) = 33.3 Hz, C_{10}, C_{12}), 132.5 (C_5), 130.4 (C_4), 126.3 (C_2), 124.8 (C_3), 125.5 (C_9, C_{13}), 123.4 (q, ^1J(C,F) = 271 Hz, *C*F_3), 123.2 (C_{11}), (C═C of alkene and C═N not observed). ^{19}F NMR (282.41 MHz, acetone-d_6): δ −63.70. Exact mass determination: found *m*/*z* 1020.2752, calcd for $C_{44}H_{41}N_2F_{18}Pt$, 1020.2730.

***N*,*N*,*N*-Triethyldeuterioammonium triflate (5).** A sample of 0.6 mL (6.8 mmol) of trifluoromethyl sulfonic anhydride was slowly added to a Schlenk tube containing 1.0 mL of D_2O. After the reaction mixture was stirred for 1 h at 21 °C, 2.0 mL of triethylamine was carefully added so that the reaction heat could be controlled. The mixture was stirred for another hour at 21 °C, after which the solvent was evaporated. The product could be recrystallized from a dichloromethane/hexanes mixture at −80 °C, yielding 0.45 g. *N*,*N*,*N*-triethyldeuterioammonium triflate as a highly hygroscopic white solid. ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 3.15 (q, J(H,H) = 7.0 Hz, 6H, CH_2), 1.28 (t, J(H,H) = 7.0 Hz, 9H, CH_3). ^{13}C NMR (75.48 MHz, CD_2Cl_2): δ 120.69 (q, J(C,F) = 318 Hz, CF_3), 47.27 (NCH_2CH$_3$), 8.67 (NCH$_2$*C*H$_3$). ^{19}F NMR (282.41 MHz, CD_2Cl_2): δ −79.80. ^{2}H NMR (76 MHz, CD_2Cl_2): δ 7.48 (br, s).

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Supporting Information Available: Information concerning the derivation of the rate law. This material is available free of charge via the Internet at http://pubs.acs.org.

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