Alkanethiolate-capped palladium nanoparticles for selective catalytic hydrogenation of dienes and trienes[†]

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Abstract

Selective hydrogenation of dienes and trienes is an important process in the pharmaceutical and chemical industries. Our group previously reported that the thiosulfate protocol using a sodium *S*-alkylthiosulfate ligand could generate catalytically active Pd nanoparticles (PdNP) capped with a lower density of alkanethio-late ligands. This homogeneously soluble PdNP catalyst offers several advantages such as little contamination *via* Pd leaching and easy separation and recycling. In addition, the high activity of PdNP allows the reactions to be completed under mild conditions, at room temperature and atmospheric pressure. Herein, a PdNP catalyst capped with octanethiolate ligands (C8 PdNP) is investigated for the selective hydrogenation of conjugated dienes into monoenes. The strong influence of the thiolate ligands on the chemical and electronic properties of the Pd surface is confirmed by mechanistic studies and highly selective catalysis results. The studies also suggest two major routes for the conjugated diene hydrogenation: the 1,2-addition and 1,4-addition of hydrogen. The selectivity between two mono-hydrogenation products is controlled by the steric interaction of substrates and the thermodynamic stability of products. The catalytic hydrogenation of trienes also results in the almost quantitative formation of mono-hydrogenation products, the isolated dienes, from both ocimene and myrcene.

Introduction

Many different homogeneous or heterogeneous catalysts have been studied for various organic reactions including hydrogenation and carbon–carbon coupling reaction.[1–3] Group VIII transition metals are usually the most common catalysts for these reactions. Moreover, palladium is more accessible and suitable for selective hydrogenation compared to other metal catalysts such as platinum and rhodium.[4,5] It is because the lower metal–hydrogen bonding energy of platinum or rhodium makes these metal catalysts readily hydrogenate multiene substrates to alkanes.[6–8] Therefore, more attention has been paid to developing palladium nanoparticles as selective hydrogenation catalysts.[9–13]

Conflicts of interest

There are no conflicts to declare.

Based on previous research work from our group, alkanethiolate-capped palladium nanoparticles generated using the thiosulfate protocol have shown good catalytic reactivity for the hydrogenation or isomerization of alkenes.[14–17] The lower surface coverage of alkanethiolate ligands on palladium nanoparticles could provide controlled poisoning for highly selective catalytic reactions. Palladium nanoparticles are still found to be stable enough to maintain homogeneous solubility for multiple recycling. Ligand-capped colloidal Pd nanoparticles are considered as semi-heterogeneous catalysts because the core contains various surface adsorption sites with different activities such as corners, edges, steps, and terraces. This characteristic of colloidal Pd nanoparticles led to their good reactivity, selectivity, facile separation and reusability, displaying the advantages of both homogenous and heterogeneous catalysts.

Freund *et al.* found out that the catalytic reaction of a terminal alkene would produce an alkane, the hydrogenation product, in a higher yield by increasing the size of Pd nano-particles.[18,19] This positive correlation strongly indicates that the hydrogenation reaction is affected by the number of terrace sites in Pd nanoparticles, which also relates to the formation of a di-σ bonded Pd–alkyl intermediate. The poisoning effect of Pd nanoparticles by thiolate ligands would play an important role in the adsorption of alkene on the metal surface. This is because the available sites in the terrace surface would decrease more for ligand-passivated nano-particles, making the hydrogenation of alkenes to alkanes more difficult to occur.

Selective hydrogenation of small dienes is an important reaction for the petroleum industry, because dienes could act as monomers for polymerization that would deteriorate fuels during pyrolysis and storage processes.[20–22] Fully saturated alkane petroleum products in a pure form are also not the most ideal since their lower boiling points and higher gas pressures would require containers with larger storage volumes. The naturally occurring trienes, ocimene and myrcene, are frequently used in the perfume industry, and the selective hydrogenation of natural triene products is also important in the pharmaceutical industry. It is because the primary product has the potential to be the precursor for functionalized compounds such as oxygenated derivatives.[23,24] Many research groups have utilized different metal complexes and hydrogen sources to reduce diene and triene compounds in various solvents using either homogeneous or heterogeneous conditions.

An octanethiolate-passivated palladium nanoparticle (C8 PdNP) catalyst has shown good reactivity for the selective hydrogenation of penta-1,4-diene, an isolated diene, to monoenes under mild reaction conditions in our previous work.[25] Building upon this previous work, in this article we investigate the catalytic applications of C8 PdNP for the selective hydrogenation of various conjugated dienes and trienes. The mechanism for the high selectivity of C8 PdNP is proposed based on kinetic studies and catalysis results for various substrates. Comprehensive comparisons with other catalytic systems on the selective hydrogenation of conjugated dienes and trienes are also presented.[12,26,27]

Results and discussion

An octanethiolate-capped Pd nanoparticle (C8 PdNP) catalyst with an average core size of ~2.3 nm is synthesized and its composition and structure are confirmed using various instruments as shown in our previous article and in the ESI.[†][25] C8 PdNP is used as the catalyst for the hydrogenation of various conjugated diene and triene substrates as shown in Table 1. The catalytic activity of C8 PdNP is directly compared with other Pd-based heterogeneous catalysts (Pd/C and Pd/Al$_2$O$_3$).

The catalytic reactions of conjugated dienes with different substitution patterns around C=C bonds (**1**–**6**) using C8 PdNP produce almost exclusively mono-hydrogenation products (MH), without having double hydrogenation products (DH). In addition, the hydrogenation of trienes (**7** and **8**) using C8 PdNP also results in high yields of isolated dienes, the mono-hydrogenation products (MH). This high selectivity of C8 PdNP for mono-hydrogenation reaction is clearly distinguishable from the catalytic results of other Pd-based heterogeneous catalysts, Pd/C and Pd/Al$_2$O$_3$, that produce mostly double-hydrogenation products (DH) from both dienes and trienes. This different reactivity confirms the important role of alkanethiolate ligands in controlling the activity of the PdNP catalyst surface. With its surface passivated by alkane-thiolate ligands, the PdNP has increased stability, so that it avoids aggregation and keeps the large surface area intact. The alkanethiolate surface ligand on the PdNP would block more active sites (terrace surfaces) for hydrogenation and promote the selective hydrogenation of dienes.

The product ratios of the 1,4- and 1,2-addition products in addition to the overall conversion yields during the kinetic study are summarized in Table 2. The catalytic reaction of C8 PdNP with 2,3-dimethyl-buta-1,3-diene **1** exhibits excellent selectivity toward the mono-hydrogenation products with 100% conversion yield. The analysis of the final monoene composition showed that the major product is 2,3-dimethyl-2-butene **1b**, the 1,4-addition product, and the minor product is 2,3-dimethyl-1-butene **1a**, the 1,2-addition product. The high yield of **1b** is the result of both the initial 1,4-addition reaction and the subsequent isomerization of the terminal alkene, the 1,2-addition product, into an internal alkene. This is clearly evidenced by the kinetic study of dienes to monoenes, which is monitored by ^{1}H NMR as shown in Fig. 1. The decreasing signals at 1.9 and 4.9 ppm in Fig. 1 indicate the consumption of compound **1**, and the increased signals at 1.7 (or 1.0) and 1.6 ppm correspond to two mono-hydrogenation products, which are the chemical shifts for **1a** and **1b**, respectively. After the first hour of reaction, the conversion of **1** reaches over 50% with the ratio of the 1,4-/1,2-addition products at 3.43. The TOF at the first hour is calculated to be 375.1 molecules per Pd per h. The consumption of reactant **1** is almost complete after 5 h of reaction with the ratio of the 1,4-/1,2-addition products at 4.9. The result of the 24 h reaction indicates that the yield of **1b** is still increasing after 5 h of reaction with the ratio of the 1,4-/1,2-addition products reaching 10.4. This is clear evidence suggesting that the isomerization of the terminal alkene **1a** to the internal alkene **1b** continuously takes place after the 5th hour of reaction. The good activity of C8 PdNP for the isomerization of terminal alkenes to internal alkenes driven by a thermodynamic effect has previously been

[†]Electronic supplementary information (ESI) available.

reported by our group.[25] The mechanistic explanation for the high selectivity to the 1,4-addition product in the 2,3-dimethyl-buta-1,3-diene **1** hydrogenation reaction is provided in Scheme 1.

In order to prove that the direct 1,4-addition is the major reaction route instead of the isomerization of the 1,2-addition product, the catalytic hydrogenation of commercially available compound **1a** is studied. The result shows the low conversion efficiency of isomerization from **1a** to **1b** with only 52% of **1a** being isomerized to **1b** after 24 h of reaction (Table 3). The slow conversion of **1a** to **1b** is partly due to the lower number of α hydrogen atoms in the mono-σ-bonded palladium alkyl intermediate generated from the adsorption of alkene **1a** on the PdNP surface. Since the terminal carbon has more hydrogen atoms than the internal α carbon, the mono-σ-bonded intermediate would most likely take the hydrogen from the terminal carbon. It would cause the intermediate to equilibrate back to the starting material, the terminal alkene. The kinetic study showing the low conversion rate of **1a** to **1b** proves that the initial direct 1,4-addition route for **1** would be the major route for the formation of **1b** and supplemented by the isomerization of the 1,2-addition product **1a**.

The selectivity between the 1,4- and 1,2-addition products is also summarized for other diene and triene substrates in Table 2. Due to the structural characteristics of substrates **3**, **5**, and **6**, generating the same products for the 1,2-addition and 1,4-addition reactions, the major reaction route for these substrates could not be identified by analysing the products. However, C8 PdNP clearly shows high selectivity for the 1,4-addition product from the reactions of 2-methylbuta-1,3-diene **2** and hexa-1,3-diene **4**. After the direct formation of both 1,4-addition product **2c** and 1,2-addition product **2a**, the isomerization of **2a** would further take place readily because of the presence of two hydrogens that can be removed from its mono-σ-bonded Pd alkyl intermediate. Though a trace amount of **2b** is observed during the first few hours of reaction, the thermodynamic stability of the isomerized product **2c** makes **2b** even easier to isomerize, completely depleting the presence of **2b** after 24 h of reaction.

For substituted buta-1,3-dienes **1** and **2**, the hydrogenation results in a higher 1,4-/1,2-addition ratio because the formation of a 1,4-di-σ-bonded intermediate for these substrates is sterically more accessible than that of other substrates with substituent groups on the 1,4-position. In addition, the isomerization of the 1,2-addition product occurs more easily because the equilibrium of isomerization would be driven by forming a more thermodynamically stable product. For the catalytic reaction of hexa-1,3-diene **4**, however, the 1,4-/1,2-addition product ratio is relatively lower than that of substituted buta-1,3-dienes. The 1,4-di-σ-bonded intermediate generated from **4** is less accessible due to the presence of an ethyl substituent group causing steric hindrance for the initial hydrogen addition. Moreover, the isomerization of **4a**, one internal di-substituted alkene, to **4c**, another internal di-substituted alkene, does not provide any additional thermodynamic enthalpy reduction eliminating a driving force for the isomerization.

The analyses of the mono-hydrogenation products generated from the hydrogenation of trienes **7** and **8** are also shown in Table 2. The presence of a large alkyl substituent group at

the diene part of ocimene **7** decreases the ratio of the 1,4- and 1,2-addition products. The yield for **7a**, the 1,2-addition product, is relatively high due to the good accessibility of the terminal alkene group to the Pd surface. Another possible 1,2-addition product **7b** does not form because of the steric interference provided by the surrounding substituent groups. The lack of a thermodynamic driving force from products **7a** to **7c** as seen from the reaction of **4** is another main reason for the decreased yields of the 1,4-addition product. The ratio of the 1,4-/1,2-addition products for the catalytic reaction of myrcene **8** is, however, more than twice higher than that of ocimene **7**. This is because both terminal carbons of the diene group do not possess any substituent group resulting in less steric interference for direct 1,4-hydrogen addition compared to ocimene **7**. The thermodynamic stability of **7c** is also higher than that of **8a** and **8b**, the more likely 1,2-addition products, making the isomerization more likely to occur. As shown in Table 2, C8 PdNP is highly selective towards the mono-hydrogenation products for both ocimene and myrcene and would not hydrogenate the highly substituted and isolated C6=C7 double bond.

C8 PdNP clearly exhibits excellent selectivity to internal alkenes, the mono-hydrogenation and 1,4-addition products, compared to other reported catalytic systems summarized in Table 4 for diene hydrogenation.[12,21,27–32] Not only are the conversion yields and selectivity superior but also the reaction conditions (room temperature and atmospheric pressure) are much friendlier than any known homogenous and heterogeneous catalysts tested for diene hydrogenation. Since both dienes and terminal alkenes are potential monomers for the polymerization reaction, C8 PdNP could either hydrogenate the dienes by a 1,4-addition reaction or isomerize terminal alkenes to internal alkenes under mild reaction conditions, so that the deterioration of petroleum products can be effectively prevented by limiting the potential polymerization in the petroleum pyrolysis process. The comparison of C8 PdNP with other catalysts used for ocimene and myrcene hydrogenation is also summarized in Table 4.[23,33] The results again confirmed the excellent activity and selectivity of C8 PdNP for the selective mono-hydrogenation of trienes to internal isolated dienes.

The stability and recyclability of C8 PdNP are tested using the catalytic reaction of 2,3-dimethylbuta-1,3-diene, **1**. C8 PdNP is precipitated and separated from the reaction mixture. The PdNP is further dried without any solvent before being recycled for additional catalysis reactions. As shown in Fig. 2, the activity and selectivity of C8 PdNP are mostly maintained especially without generating any double hydrogenation product even after 7 cycles. The conversion of the reactant after 7 cycles is still above 95% and the selectivity for the 1,4-addition product remains over 80% after 7 catalytic cycles. To examine the leaching of Pd atoms from C8 PdNP during the catalytic reaction, the presence of Pd^{2+} in the crude solution is determined using ICP-AES. The results suggest that the digested product solution has only ~0.0546 ppm Pd^{2+}, which shows the overall high stability of C8 PdNP during the hydrogenation reaction.

Conclusions

Octanethiolate-capped palladium nanoparticles show excellent activity and selectivity for the mono-hydrogenation of dienes into internal alkenes and trienes into isolated internal dienes. The kinetic study and comparison of various catalysis reactions indicate that the conjugated

diene hydrogenation reactions mainly involve the direct 1,4-addition reaction in addition to the isomerization of the 1,2-addition product that further isomerizes terminal alkenes into internal alkenes. The leaching examination and recycling study of the octanethiolate-capped palladium nanoparticles show the high stability of the catalyst. This octanethiolate-capped palladium nanoparticle catalyst, therefore, has high technological potential for effective elimination of reactive monomers such as dienes and terminal alkenes for polymerization and prevention against the deterioration of crude oil storage.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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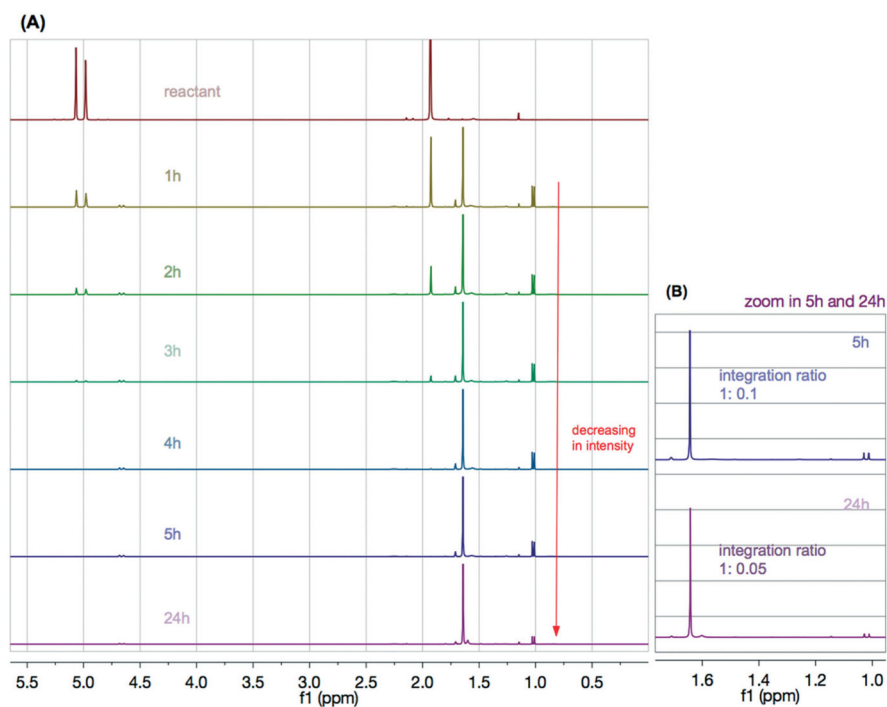
Fig. 1.
(A) Kinetic study of 2,3-dimethylbuta-1,3-diene **1** hydrogenation using C8 PdNP at room temperature under 1 atm H_2 in $CDCl_3$. (B) The zoom is for the area of the 5 and 24 h spectra. Chemical shifts of compound **1a** are at 1.02 ppm (–CH_3) and 1.71 ppm (allylic-CH_3). Chemical shift for compound **1b** is at 1.64 ppm (–CH_3).

Recycle Study

■ 1,2-add% ■ 1,4-add% ■ reactant%
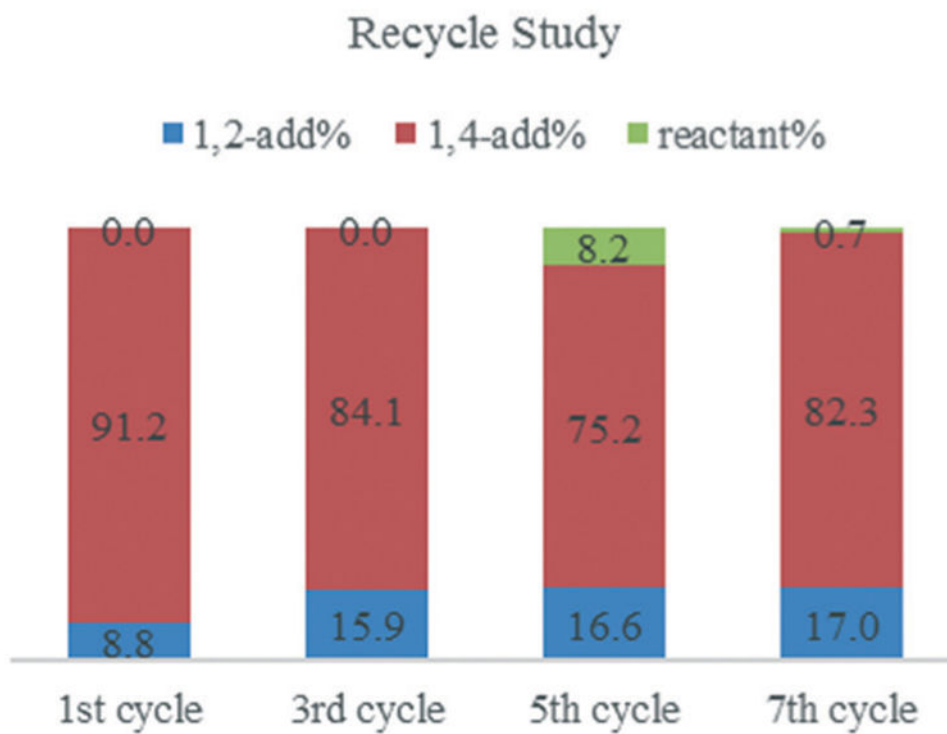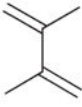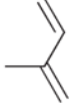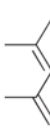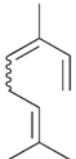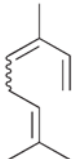
Fig. 2.
The recycle study of 2,3-dimethylbuta-1,3-diene **1** hydrogenation using C8 PdNP. Reaction conditions: 0.5 mmol diene, 5 mol% Pd catalyst, 2.5 mL CDCl$_3$, 1 atm H$_2$, 24 h reaction. Yields were obtained by 400 MHz NMR.
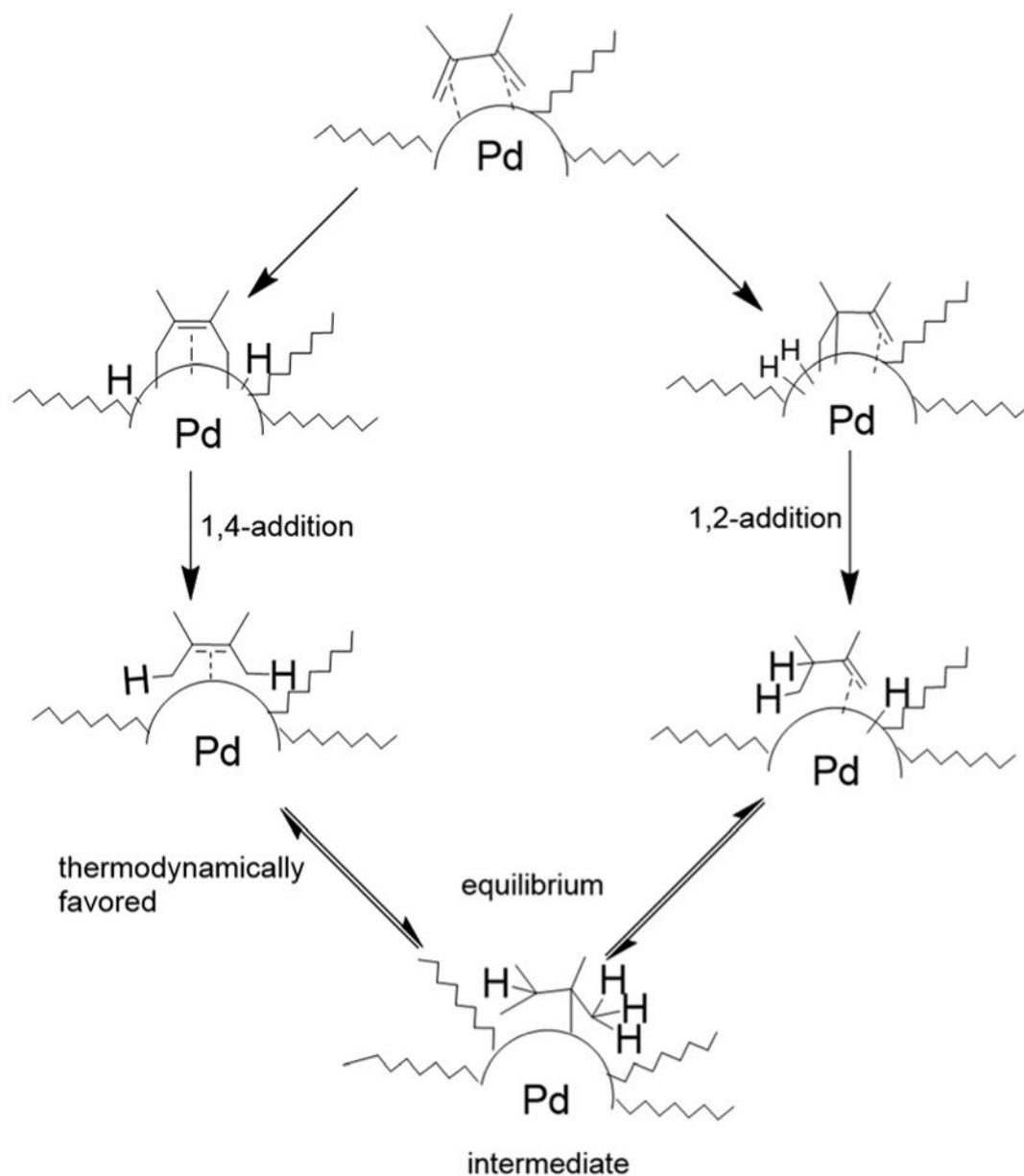
Scheme 1.
Proposed mechanism for the catalytic reaction of 2,3-dimethylbuta-1,3-diene **1** with octanethiolate-capped Pd nanoparticles.

Table 1

Catalysis results of various dienes and trienes with the octanethiolate-capped Pd nanoparticle catalyst, Pd on carbon, and Pd on alumina in $CDCl_3$ at 1 atm H_2 after 24 h[a]
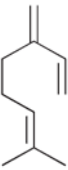
Substrate	C8 PdNP		Pd/C		Pd/Al$_2$O$_3$	
	MH[b]	DH[b]	MH[b]	DH[b]	MH[b]	DH[b]
1	100%	0%	0%	100%	0%	100%
2	100%	0%	0%	100%	0%	100%
3	100%	0%	0%	100%	—[c]	—[c]
4	100%	0%	0%	100%	0%	100%
5	97%	3%	9%	91%	6%	94%
6	95%	0%	0%	100%	0%	100%
7	100%	0%	0%	100%	0%	100%

Substrate	C8 PdNP		Pd/C		Pd/Al$_2$O$_3$	
	MH[b]	DH[b]	MH[b]	DH[b]	MH[b]	DH[b]
8	92%	0%	4%	96%	10%	90%
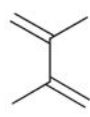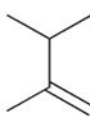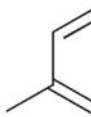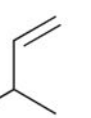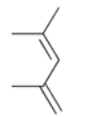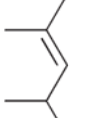
[a]Reaction conditions: 0.5 mmol diene, 5 mol% Pd catalyst, 2.5 mL CDCl₃, 1 atm H₂, 24 h reaction. Other heterogeneous catalysts, Pd/C and Pd/Al₂O₃, were also examined under the same reaction conditions. Yields were obtained by 400 MHz NMR.
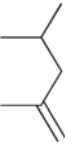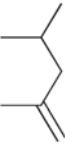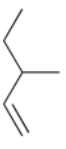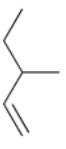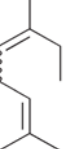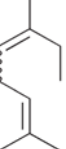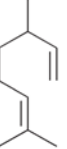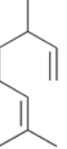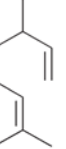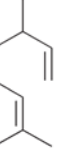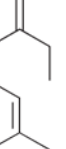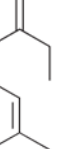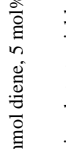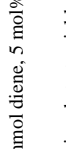
[b]Mono-hydrogenation (MH), double-hydrogenation (DH).

[c]Not attempted.

Table 2

Hydrogenation of different diene and triene substrates using C8 PdNP[a]

Substrate	1,2-Add	Yield (%)	1,4-Add	Yield (%)	1,4-Add/1,2-add
1	**1a**	9	**1b**	91	10.4
2	**2a**	7	**2c**	93	14.2
	2b	0			
3[b]	**3a**	92[c] E/Z = 4.0	**3a**	—	—
	3a	8			
4	**3b**	29	**4c**	71 E/Z = 3.5	2.4
	4a	0			
	4b				
5[b]	**5a**	90[c]	**5a**	—	—
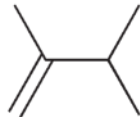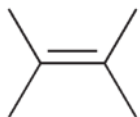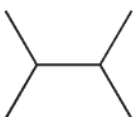
Substrate	1,2-Add	Yield (%)	1,4-Add	Yield (%)	1,4-Add/1,2-add
6[b]	5b	7			
	6a	90[c]	6a	—	—
	6b	5			
7	7a	41	7c	59	1.5
	7b	0			
8	8a	3	7c	69	3.0
	8b	20			

Table 3

Hydrogenation of 2,3-dimethylbut-1-ene with the C8 PdNP catalyst[a]
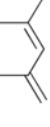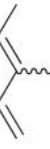

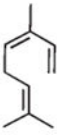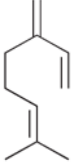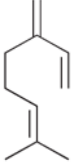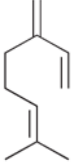| Time	Terminal alkene (%)	Internal alkene (%)	Alkane (%)
1 h	88%	12%	0%
3 h	78%	22%	0%
6 h	66%	34%	0%
24 h	48%	52%	0%
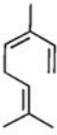
[a]Reaction conditions: 0.5 mmol diene, 5 mol% Pd catalyst, 2.5 mL CDCl3, 1 atm H2, 24 h reaction. Yields were obtained by 400 MHz ^{1}H NMR.

Table 4

Comparison table for the catalytic hydrogenation selectivity of dienes and trienes

Substrate	Catalyst	Reaction pathway[b]	Conv[b]	MH[b]	DH[b]	1,2-Add	1,4-Add	Internal alkene	Reaction conditions
	C8 PdNP	Semi-HET	100%	100%	0%	8.8%	91.2%	91.2%	R.T., CDCl$_3$, 1 atm H$_2$
	PhCOOMeCr(CO)$_3$ (ref. 27)	HOM	100%	100%	0%	18%	82%	82%	160 °C, n-heptane, 30 atm H$_2$
	Pd/sgPF$_6$ (ref. 12)	Semi-HET	>99%	100%	0%	19%	81%	81%	40 °C, CH$_2$Cl$_2$, 4 bar H$_2$
	C8 PdNP	Semi-HET	100%	100%	0%	6.6%	93.4%	93.6%	R.T., CDCl$_3$, 1 atm H$_2$
	Silica polyamine PdNP composite[21]	HET	100%	94%	6%	46.5% **2a**: 24.5% **2b**: 22%	47.5%	47.5%	70 °C, toluene, 3 MPa H$_2$
	Pd/sgPF$_6$ (ref. 12)	Semi-HET	>99%	100%	0%	25% **2a**: 18% **2b**: 7%	75%	75%	40 °C, CH$_2$Cl$_2$, 4 bar H$_2$
	C8 PdNP	Semi-HET	100%	100% **3a**: 92% **3b**: 8%	0%	—	—	98.2%	R.T., CDCl$_3$, 1 atm H$_2$
	Co$_3$O$_4$ (ref. 28)	HET	39.3%	39.3% **3a**: 31.1% **3b**: 8.2%	0%	—	—	31.1%	R.T., P = 50–60 C$_5$H$_8$ mmHg, P/P = 2–3 H$_2$ C$_5$H$_8$
	[Cp$_2$ZrH(CH$_2$PPh$_2$)]$_n$ (ref. 29)	HOM	100%	0%	100%	—	—	0%[a]	80 °C, hexane/THF, 40 bar H$_2$
	C8 PdNP	Semi-HET	100%	100%	0%	29.3% **4a** only	70.7%	100%	R.T., CDCl$_3$, 1 atm H$_2$
	PhCOOMeCr(CO)$_3$ (ref. 27)	HOM	100%	100%	0%	24% **4a**: 18% **4b**: 6%	76%	94%	160 °C, n-heptane, 30 atm H$_2$
	C8 PdNP	Semi-HET	100%	96.6% **5a**: 90.3% **5b**: 6.3%	3.4%	—	—	90.3%	R.T., CDCl$_3$, 1 atm H$_2$
	Polystyrene coated PdNP on SiO$_2$ (ref. 30)	HET	>99.7%	>99.6% **5a**: 80.1% **5b**: 19.8%	0.1%	—	—	80.1%	Supercritical CO$_2$, 3 MPa H$_2$
	Dendrimer Pd complex[31]	HOM	>99%	>99% **5a**: 57% **5b**: 43%	0%	—	—	57%	25 °C, MeOH, 14 p.s.i. H$_2$
	C8 PdNP	Semi-HET	95%	95% **6a**: 90.6% **6b**: 4.1%	0%	—	—	90.6%	R.T., CDCl$_3$, 1 atm H$_2$
	Pd ferrocenyl complex[32]	—	87.1%	82.4% **6a**: 82.4% **6b**: 4%	0.7%	—	—	82.4%	R.T., acetone, 80 p.s.i. H$_2$

Substrate	Catalyst	Reaction pathway[b]	Conv[b]	MH[b]	DH[b]	1,2-Add	1,4-Add	Internal alkene	Reaction conditions
	C8 PdNP	Semi-HET	100%	100%	0%	40.8% **7a** only	59.2%	100%	R.T., CDCl$_3$, 1 atm H$_2$
	Copper–chromium oxide[33]	HET	100%	85%	15%	78% **7a**: 58% **7b**: 20%	7%	65%	140 °C, *trans*-decalin, 1 atm pressure
	C8 PdNP	Semi-HET	92.2%	92.2%	0%	23.2% **8a**: 3.1% **8b**: 20%	69%	92.2%	R.T., CDCl$_3$, 1 atm H$_2$
	Sol/gel 3% Pd/SiO$_2$ (ref. 23)	HET	96%	93.1%	2.9%	33.6% **8a**: 19.2% **8b**: 14.4%	59.5%	59.5%	80 °C, 20 atm, H$_2$ cyclohexane
	Copper–chromium oxide[33]	HOM	100%	100%	0%	92% **8a**: 23% **8b**: 69%	8%	8%	140 °C, *trans*-decalin, 1 atm pressure

[a] The data are chosen from the best selectivity results for each type of catalyst.

[b] Abbreviations for the reaction pathway: semi-heterogeneous (Semi-HET), homogeneous (HOM), heterogeneous (HET). Conversion (Conv). Mono-hydrogenation (MH), double-hydrogenation (DH).