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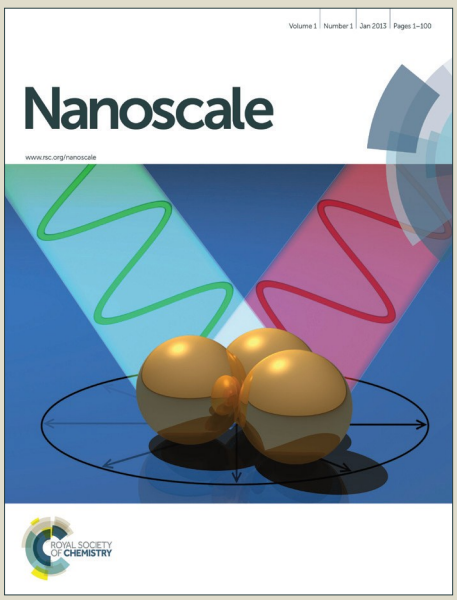

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ARTICLE

Mechanistic Interpretation of Selective Catalytic Hydrogenation and Isomerization of Alkenes and Dienes by Ligand Deactivated Pd Nanoparticles

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Unsupported thiolate-capped palladium nanoparticle catalysts are found to be highly substrate-selective for alkene hydrogenation and isomerization. Steric and poisoning effects from thiolate ligands on the nanoparticle surface contr reactivity and selectivity by influencing alkene adsorption and directing either di-σ or mono-σ bond formation. The presence of overlapping p orbitals and α protons in alkenes greatly influences the catalytic properties of deactiv palladium nanoparticles leading to easily predictable hydrogenation or isomerization products.

Introduction

Alkene transformation reactions significantly impact industrial processes, including those utilized for pharmaceutical, polymer, and petrochemical synthesis.[1,2] Diene transformations represent an especially interesting problem due to the similar reactivity of both alkenes.[3,4] To overcome this problem, synthetic methods utilizing alkene masking and modification of the other alkene followed by demasking have been demonstrated.[5-8] Despite the value of these methods, protection-deprotection is generally atom inefficient and lengthens synthesis by at least two steps. In terms of catalytic hydrogenation, metal complexes such as Wilkinson's[9,10] or Crabtree's[11,12] catalysts and various Pd complexes[13-15] are very efficient for regioselective or chemoselective hydrogenation. However, their ligand dissociation mechanism and the risk of residue metal toxicity limit their modern synthetic utility,[16,17] especially in pharmaceutical applications. Palladium based catalytic materials circumvent some of these challenges and have been adopted by many industries.[1,2] One of the most challenging problems associated with palladium, however, has been the poisoning and deactivation of these materials.[18-21]

Recently, the use of nanomaterials as catalysts gained significant attention owing to their enhanced catalytic activity and recyclability. Many groups have taken advantage of functionalized supports and ligands or designer surfactants to tune the properties of various nanomaterials.[22,23] Our laboratory demonstrated that the catalytic activity and recyclability of palladium nanoparticles (PdNP) can be controlled with thiolate-capping agents by selectively converting allyl alcohol to propanal via isomerization instead of 1-propanol via hydrogenation.[24-26] Our previous work al demonstrated that the isomerization mechanism occu through π coordination followed by the formation of a mono-σ Pd-alkyl intermediate.[27,28] With this type of mechanism i mind, the application of these PdNP catalysts for alken transformation reactions is further exploited. Herein, this paper reports a new discovery showing the influence thiolat ligands on PdNP surfaces have on substrate adsorption and surface hydrogen reactivity, leading to selective hydrogenatio or isomerization of dienes and monoenes.

Results and discussion

Supported bare PdNPs and various Pd complexes are known to hydrogenate pentene isomers (Table 1).[29-33] It is well kno n that higher alkenes such as pentene are known to only undergo complete hydrogenation via the di-σ-bonded species on palladium surfaces.[34,35] However, when 1-pentene (**1**) wa subjected to unsupported, octanethiolate-capped PdNP (2.6 ± 1.1 nm, 0.52 surface ligands/Pd surface atoms) in $CDCl_3$ und H_2 conditions for 24 hrs, the isomerization product (2-penten **2**) with only minimal amounts of pentane (**3**) was observed (entry 1). When H_2 was replaced with N_2 as a contr experiment, the catalytic con version of 1-pentene did no occur (entry 2). $SilPdCl_2$ is the only catalyst with somewha similar catalytic activity to PdNP (entry 5), however i completely loses its catalytic ability upon expo sure to air.[3 The lack of reaction in the absence of H_2 shows tha isomerization cannot be due to the π allyl mechanism becaus that reaction mechanism does not require H_2 to proceed Instead, isomerization of 1-pentene (**1**) on these PdNPs mus occur through the mono-σ bonded Pd-alkyl intermediat followed by *β*-hydride elimination as we previous proposed.[27,28] This mechanism is consistent with *trans*-2

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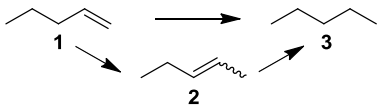
pentene hydrogenation on Pd/Al_2O_3 under ultrahigh-vacuum conditions.[34] Since **2** reluctantly reacted with thiolate-capped PdNP, it is likely that the thiolate ligands are preventing the di-substituted alkene from forming the prerequisite di-σ-bonded species for hydrogenation. On large supported bare PdNP catalysts, catalytic activity is heavily reduced over time because the alkene substrate forms too many strong di-σ-bonded species on the catalytic surface.[18,19] The thiolate capping agents on our PdNP catalyst help reduce substrate oversaturation, thereby limiting the poisonous effects.[27,28] The presence of partial PdS_x layer on the surface of PdNP after thiolate monolayer formation, which has been observed by others, might also be the reason for deactivation of PdNP catalyst.[36]

Table 1. Hydrogenation and isomerization of 1 by Pd catalysts.[a]

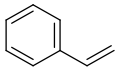
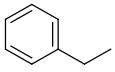
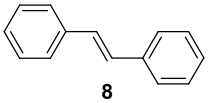
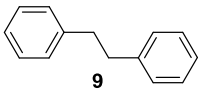
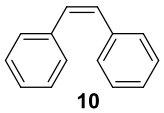
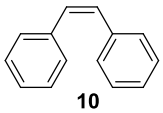
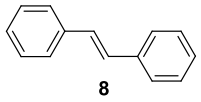
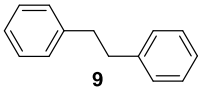
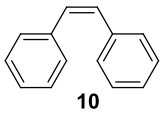
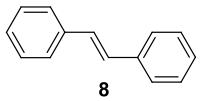
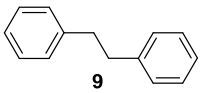


Entry	Pd Source	Time (h)	H_2 (atm)	**1** (%)	**2** (%)	**3** (%)
1	PdNP	24	1	1	90	9
2	PdNP	24	0[b]	100	0	0
3[c]	Pd Black	2	1	0.2	1.4	98.4
4	Pd/Al_2O_3	1	2	80	4	16
5	$SilPdCl_2$	4	1	1.5	71.3	27.2
6	$Pd/SiO_2/ZrO_2$	0.3	19.7	6	0	94
7	$Pd_2(OEt\text{-}T)_2Cl_2$	<0.5	1	5	45	50

[a] 25°C. [37] [b] N_2. [c] flow reactor.

To understand whether hydrogenation could be forced to occur by blocking isomerization (Table 2), 3,3-dimethylbut-1-ene (**4**) and styrene (**6**) were subjected to PdNP under H_2 conditions. No reaction between PdNP and **4** took place (entry 1) while **6** was completely converted to ethylbenzene (entry 2). Even though styrene's steric bulk is quite considerable, the p orbitals and planar geometry of the benzene ring must be aiding di-σ-bond formation, which allows hydrogenation to proceed. Comparatively, the t-butyl group in **4** does not contribute to, but hinders di-σ-bond formation, preventing hydrogenation to take place. The effect of substitution pattern around nonaromatic sp^2 carbons was also studied using isomers of stilbene. Under the same reaction conditions, both *trans*-stilbene (**8**) and *cis*-stilbene (**10**) were hydrogenated to 1,2-diphenylethane (**9**) with 4% and 9% conversion, respectively. While no isomerization of **8** was observed (entry 3), partial isomerization (29 %) of **10** to **8** (*cis* to *trans*) clearly took place (entry 4). Concerned that the isomerization of **10** was taking place due to ambient light,[36-38] a control experiment without PdNP was performed and no isomerization resulted. By extending the reaction time to 48 hrs with additional H_2 after 24 hrs, **10** was converted to a mixture of 54% isomerization product (**8**) and 21% hydrogenation product (**9**) (Figure S3). Because of stilbenes (**8** and **10**) being bulkier than styrene (**6**), the extended *p* orbital overlap from two benzene rings would not be enough to allow **8** and **10** to be hydrogenated with higher conversion. Furthermore, the preference of isomerization over hydrogenation for **10** is strongly indicative of the formation of mono-σ bonded Pd-alkyl species. As the steric bulk of these species increases, the addition of the second H atom must be slower than the isomerization of *cis* to *trans* on PdNP surface.

Table 2. Isomerization and hydrogenation by PdNP.[a]

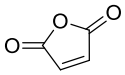
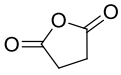
Entry	Substrate	Product	Conv (%)
1			0
	4	5	
2			99
	6	7	
3			4
	8	9	
			0
		10	
4			29(0)
	10	8	
			9(0)[b]
		9	
5			54[c]
	10	8	
			21[c]
		9	

[a] Reaction conditions: 50 mL round bottom flask, alkene (0.5 mmol), PdNP (5 mol%), $CDCl_3$ (2.5 mL), H_2 (1 atm), 24 h. [b] No PdNP was used. [c] 48 h reaction time with H_2 added after first 24 h.

Further expansion of the substrate scope of the thiolate capped PdNPs was attempted using cyclic alkenes (Table 3). First, the hydrogenation of cyclohexene (**11**) was examined and as expected, only a low 5% conversion to cyclohexane (**12**) was obtained (entry 1). In the case of 1,4-cyclohexadiene (**13**), 33% conversion to **11** resulted (entry 2). Its isomerization product, 1,3-cyclohexadiene, was not observed. This is likely due to the near planar geometry of **13** which allows all of its *p* orbitals to contribute to di-σ bond formation. Instead of

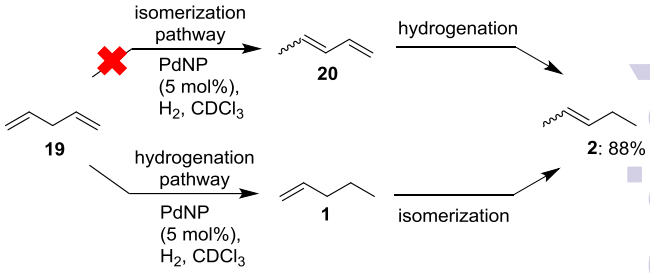
forming the mono-σ bonded species and undergoing isomerization, this geometry makes the direct addition of both H atoms possible. Conjugation with carbonyls was also considered. For 2-cyclohexenone (**15**), only the alkene was expected to be hydrogenated because thiolate-capped PdNPs are not active enough to reduce carbonyls.[24-26] Indeed, **15** underwent 83% conversion to cyclohexanone (**16**) (entry 3). Similarly, maleic anhydride (**17**) was hydrogenated to succinic anhydride (**18**) with 64% conversion after 24 hrs. Extending the reaction time to 48 hrs, with hydrogen gas added after the first 24 hrs, increases the conversion to 87% (entry 4). Even though the conversions of these cyclic alkenes range from 33%-83% after 24 hrs, the selectivity remains excellent in all cases.

Table 3. Isomerization and hydrogenation by PdNP.[a]

Entry	Substrate	Product	Conv (%)	Selectivity (%)
1	 **11**	 **12**	4	--
2	 **13**	**11** **12**	33 <1	>99 <1
3	 **15**	 **16**	83	>99
4	 **17**	 **18**	64 87	>99 >99[b]

[a] Reaction conditions: 50 mL round bottom flask, alkene (0.5 mmol). PdNP (5 mol%), $CDCl_3$ (2.5 mL), H_2 (1 atm), 24 h. [b] 48 h, H_2 added after 24 h.

Next, the reactivity of isolated dienes with PdNP was investigated. In contrast to stilbene, a pentadiene system is not as sterically hindered while still having strong interaction with the PdNP surface. It was projected that symmetric 1,4-pentadiene (**19**) might first isomerize to conjugated 1,3-pentadiene (**20**), followed by hydrogenation of the terminal alkene, forming 2-pentene (**2**) (Scheme 2). Alternatively, it was also possible that **19** would be directly hydrogenated to 1-pentene without the intermediate **20**, similar to 1,4-cyclohexadiene (13).



Scheme 1. Possible pathways to **2**.

The reaction progress was followed with ^{1}H NMR spectroscopy (Fig. 1). The gradual decrease in the αCH_2 signals at ~2.8 ppm of **19** directly correlates to the consumption of **19**. Since the characteristic vinyl proton signals at 6-7 ppm of **20** are not observed while the new characteristic αCH_2 signals at ~1.7 ppm of **1** is detected, the hydrogenation pathway must be the mechanism by which **2** forms. Therefore, we propose the mechanism (Fig. 2) of 1,4-pentadiene (**19**) isomerization and hydrogenation to 2-pentene (**3**) on thiolate-capped PdNP to be direct di-σ-bond formation after substrate adsorption via two Pd-π bond formation. This allows two hydrogen atom insertions to occur simultaneously, resulting in the formation of **1** from the di-σ bonded intermediate **A**. With only a single alkene moiety, **1** can either desorb or isomerize to **2** via mono-σ bonded Pd-alkyl intermediate **C**. This is followed by β-hydride reductive elimination to form Pd-π bond intermediate **D** and **2** desorbs to create free space on the PdNP surface to restart the catalytic cycle.

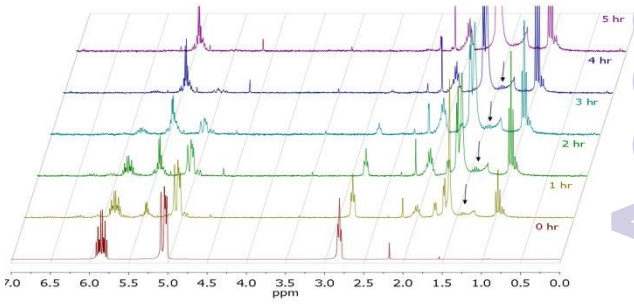


Fig. 1 ^{1}H NMR of **19** conversion to **2** over time.

Isolated dienes with αCH_2 such as 1,4-cyclohexadiene (**13**) and 1,4-pentadiene (**19**) were directly hydrogenated without initial isomerization while larger activated alkenes such as stilbenes (**8** and **10**) were much less reactive, with **10** preferring *cis*-to-*trans* isomerization over hydrogenation. It

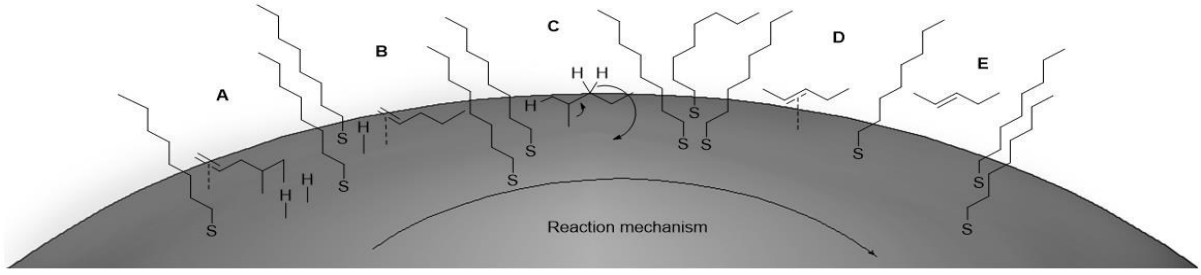
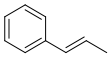
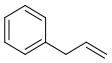
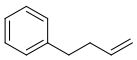


Fig. 2 Proposed mechanism of **19** reacting with PdNP.

would therefore be interesting to examine the reactivity of alkenes with both an activating phenyl ring and αCH_2 (Table 4). trans-β- Methylstyrene (**21**) only underwent 10% conversion (entry 1) while allylbenzene (**22**) underwent 92% conversion (entry 2). This result confirms a low reactivity of di-substituted alkenes, especially trans-alkenes, for the catalytic reaction of deactivated PdNPs. The conversion of 1-phenyl-3-butene (**23**) was >99% with 96% selectivity for its isomerization products (entry 3), 1-phenyl-1-butene (**25**) and 1-phenyl-2-butene (**26**), with the selectivity of 13% and 87%, respectively.

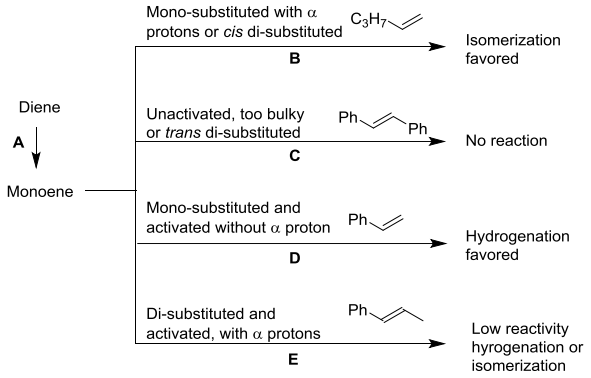
Table 4. Benzene and αCH_2 containing alkene hydrogenation by PdNP.[a]

Entry	Substrate	Conv (%)	Isomerization (%)	Hydrogenation (%)
1	 **21**	10	23	77
2	 **22**	92	91[b]	9
3	 **23**	>99	96[c]	4

[a] Reaction conditions: 50 mL round bottom flask, alkene (0.5 mmol), PdNP (5 mol%), $CDCl_3$ (2.5 mL), H_2 (1 atm), 24 h. [b] 91% trans-**21**, 9% cis-**21**. [c] 10% *trans*-**25**, 3% *cis*-**25**, 68% *trans*-**26**, 19 % *cis*-**26**.

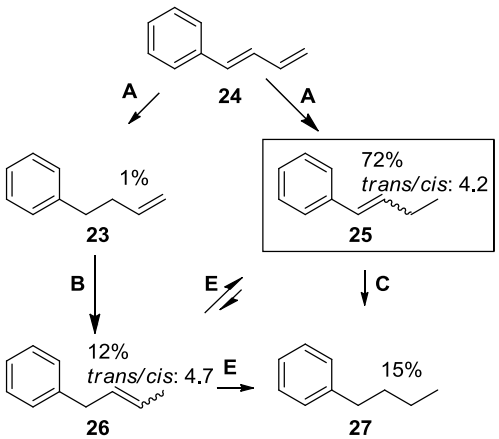
The results showed that the proportion of isomers in the equilibrium mixture of alkenes depended largely on the structure of starting alkenes as indicated by the isomerization of **22** and **23** to the corresponding disubstituted alkenes. The ratio of *trans/cis* isomers for the reaction of **22** was 10.1, which was much greater than the *trans/cis* ratio for the reaction of **23** (the *trans/cis* ratio of **25** and **26** were 2.7 and 3.5, respectively). This indicated the location of phenyl group near β-H elimination site might decrease the activation energy for more thermodynamically stable *trans* products. The overall results prove that the deactivated PdNPs favor single isomerization of mono-substituted alkenes to trans-di-substituted alkenes. Despite the steric bulk of the benzene ring, the reactivity of these 1-phenyl, α-proton containing alkenes (**22** and **23**) on PdNP is comparable to the reactivity of terminal monoalkenes, such as 1-pentene (**1**) producing mostly isomerization products.

In general, acyclic alkenes hydrogenation or isomerization can be predicted (Scheme 5). Diene directly hydrogenates to monoene without isomerization; monoene's reactivity with PdNP depends on its structure. If it is mono-substituted with αCH_2 (**1**,**22**,**23**) or cis di-substituted (**10**), isomerization is favored. If it is both unactivated and too bulky (**4**) or trans di-substituted (**8**,**21**), low reactivity is predicted. If it is mono-substituted but activated and does not contain αCH_2 (**6**), hydrogenation occurs.



Scheme 2. Expected reactivity of alkenes on PdNP.

To test these predictions, the reactivity of 1-phenyl-trans-1,3-butadiene (**24**) was examined. This is an interesting diene due to the presence of two activated alkenes capable of being hydrogenated. Based on the generalizations, **24** will undergo one hydrogenation event, forming **25** with small amounts of **23**. Mono-substituted **23** with αCH_2 will then isomerize to **26**, which can further isomerize to **25**. As a result, the monoene major product expected is di-substituted monoene **25**. Indeed, GC/MS analysis after 24 h reaction reveals that the reaction was 72% selective for **25**, with a *trans/cis* ratio of 4.2. Its isomer **26** was produced in 12% with a *trans/cis* ratio of 4.7 (Scheme 6). **24** underwent 15% conversion to the complete hydrogenation product **27** via both **25** (major) and **26** (minor) as intermediates. In comparison, **21** underwent only 8% conversion to its corresponding hydrogenation product. The increased hydrogenation activity for **24** compared to **21** can be accounted for by the better p orbital overlap of **24**, which allows it to be adsorbed closer to the surface of PdNP initially.



Scheme 3. Isomerization and hydrogenation products of **24**.

Conclusions

We have taken advantage of the specific di-σ bond that must form with Pd surface before hydrogenation takes place in higher alkenes. Thiolate ligands prevent sterically hindered substrates from forming these di-σ bonds unless the substrate has good *p* orbital overlap capable of forming multiple Pd-π

bond interactions. After a single hydrogenation in these substrates, only π interactions can be made with PdNP due to the loss of p orbital overlap, discouraging subsequent hydrogenation from occurring. Even though isomerization can still take place via mono-σ bonded intermediates, this can be exploited in order to selectively synthesize di-substituted internal alkenes.

Acknowledgements

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