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Alkene Isomerization by “Sandwich” Diimine-Palladium Catalysts

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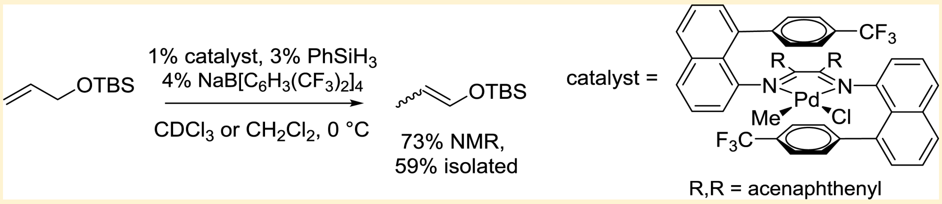
S *Supporting Information*



ABSTRACT: In contrast to traditional diimine-palladium complexes, sterically hindered “sandwich” diimine-palladium adducts act as olefin isomerization catalysts. Terminal olefins are selectively converted to 2-olefins by a sequence of migratory insertion, β-hydride elimination, and olefin displacement. The reaction is performed at 0 °C with 1 mol % of an air-stable precatalyst and tolerates functional groups such as ketones, silyl ethers, and halogens. The isomerization may be used to produce silyl enol ethers from protected allylic alcohols.

Late transition metal-catalyzed olefin polymerization by bulky α-diimine-supported nickel and palladium catalysts **1** and **2** has been extensively investigated (Figure 1).[1] These complexes polymerize ethylene and α-olefins to high-molecular weight polymers. Palladium catalysts afford hyperbranched polymers, while the properties of material obtained by nickel catalysts depend on the monomer concentration and temperature. More recently, sandwich catalysts of type **3** and their nickel analogues have been investigated for ethylene and α-olefin polymerization.[2]

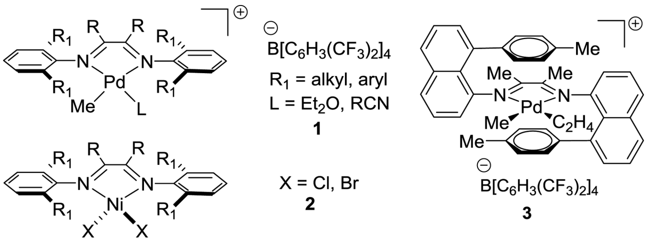
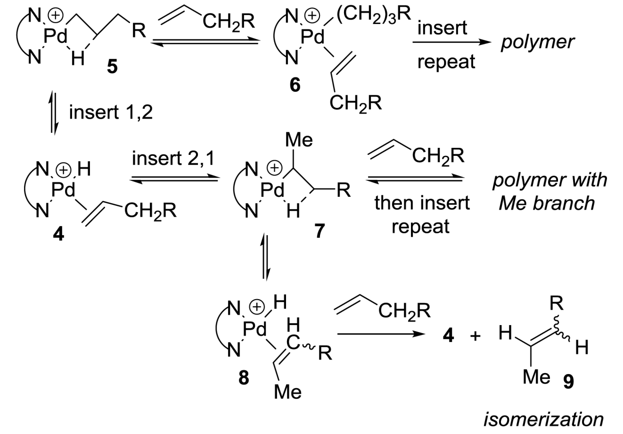


Figure 1. Diimine catalysts.

The unique feature of the diimine catalysts that allows production of branched polymer starting from ethylene and chain-straightened material from α-olefins is referred to as “chain-walking”.[3a] Mechanistic details of this phenomenon are shown in Scheme 1 and lead to the conclusion that, if certain conditions are met, these complexes should be capable of acting as efficient olefin isomerization catalysts. Migratory insertion of palladium hydride **4** affords either linear palladium alkyl agostic species **5** or a branched complex **7**. Agostic complexes of type **5** react with an α-olefin to give alkyl palladium species of type **6**, the resting state(s) in polymerization. Alternatively, branched agostic species of type **7** can bind olefin; migratory insertion then affords a methyl branch in the polymer. β-Hydride elimination from **7** can yield **8**, where the double bond has migrated into the alkyl chain. If the bound internal olefin in **8** is displaced, **4** is regenerated together with isomerized olefin **9**. Barriers to β-hydride elimination (**5** to **4** or **7** to **8**) leading to olefin hydride complexes are ca. 7 kcal/mol. The ability to switch from a polymerization to an isomerization manifold should be a function of the rate of chain-running and olefin displacement (**8** to **4** and **9**) vs migratory insertion rates in palladium alkyl olefin complexes such as **6**. Ethylene migratory insertion barriers in **1** (L = C_2H_4) are about 17 kcal/mol at −30 °C, whereas, in **3**, they are 19.4 kcal/mol at −25 °C.[2b,3a,b] Additional steric hindrance at the reactive center in **3** (relative to that in **1**) should result in weaker binding of bulky internal olefin **9** with respect to the less hindered α-olefin.

Scheme 1. Mechanistic Considerations



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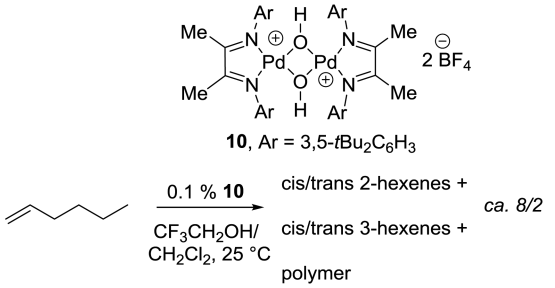
Consequently, under certain conditions, catalysts of type **3** may act as olefin isomerization catalysts. Examination of the literature shows that cationic palladium-diimine **10** acts as a catalyst for α-olefin isomerization and oligomerization, with TOFs of about 2100 and 200 h^{-1} at 25 °C, respectively (Scheme 2).[3c] We speculated that palladium sandwich complexes might act as olefin isomerization catalysts as well. Furthermore, due to the expected weak binding of bulky internal olefins to the palladium center crowded by extremely bulky sandwich ligands, we expected that regioselective olefin isomerization might be possible. We report here that terminal olefins are selectively converted to 2-olefins by using sandwich diimine-palladium catalysts at low temperatures. This procedure allows for a simple and efficient synthesis of aldehyde-derived silyl enol ethers from silylated allylic alcohols.

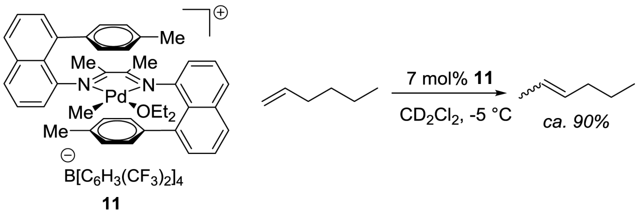
Scheme 2. Olefin Isomerization by Palladium-Diimine Complexes

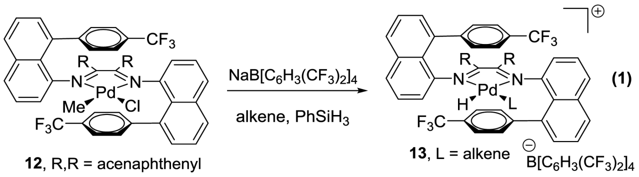


A number of olefin isomerization catalysts have been reported in the literature.[3c,4−8] Grotjahn has developed bifunctional ruthenium catalysts that selectively isomerize 1-alkenes to *Z*-2-alkenes.[4] For several substrates, catalyst loadings as low as 0.05 mol % were employed. Rhodium, iridium, and iron catalysts have also been used for olefin isomerization.[5] Several investigators report cobalt-catalyzed alkene isomerizations.[6] Most relevant to this investigation, a number of palladium complexes were shown to catalyze olefin isomerization.[3c,7] As described earlier, Bercaw has shown that cationic palladium-diimine catalysts possessing 3,5-di-*t*-butylphenyl substituents isomerize 1-hexene to a mixture of 2- and 3-hexenes. Additionally, a substantial amount of hexene polymerization is observed. The catalysis is initiated via C−H activation, followed by Wacker oxidation, to afford an active palladium hydride.[3c] Lindhardt, Skrydstrup, and Gooßen have employed tri-*t*-butylphosphine-containing palladium catalysts for transformation of 1-alkenes to 2-alkenes.[7b,c] Li and Xu have used a palladium hydride, generated in situ from $PdCl_2(PPh_3)_2$ and $(EtO)_3SiH$, to convert 4,4-diaryl-1-butenes to corresponding 2-alkenes. Several other transformations include olefin double-bond isomerization as one of the key steps.[8]

In the initial experiment, ca. 15 equiv of 1-hexene was added to complex **11** in CD_2Cl_2 at −78 °C (Scheme 3). Following warming to −5 °C, nearly complete isomerization to a mixture of *trans*- and *cis*-2-hexenes was observed in about 1.5 h. Only minor amounts of hexene oligomers and 3-hexene were detected. The initial rates of 1-hexene disappearance at different initial concentrations of the olefin at 268 K were examined and showed a clear dependence on 1-hexene concentration (see the Supporting Information for details). The first-order rate constant for the isomerization of 1-hexene, $k = 8\cdot10^{-4}$ s^{-1}, corresponds to $\Delta G^{\ddagger}$ = 19.4 kcal mol^{-1}. This barrier is comparable to that for ethylene migratory insertion in palladium sandwich-diimine complex **3**.[2b] The experiment shows that selective isomerization of terminal olefins to 2-olefins by using palladium sandwich diimine complexes should be feasible. However, use of complex **11** as a catalyst is problematic since **11** is unstable at ambient temperatures. Hence, a more convenient procedure was used involving activation of stable precatalyst **12** by *in situ* treatment with $NaB[C_6H_3(CF_3)_2]_4$ and $PhSiH_3$. This procedure is expected to generate an active cationic palladium hydride **13** according to earlier literature precedent (eq 1).[9]

Scheme 3. 1-Hexene Isomerization by 11





(1)

Results of isomerizations of a variety of olefins are summarized in Table 1. The precatalyst **12** is activated with 3 mol % phenylsilane and 4 mol % sodium tetraarylborate. Reactions are carried out in $CDCl_3$ at 0 °C. 1-Hexene is isomerized to a 2.1/1 mixture of *trans*- and *cis*-2-hexenes (entry 1). After termination of the isomerization, the reaction mixture contains also 7% of 3-hexenes and 1.5% of 1-hexene. Methylenecyclohexane is isomerized to trisubstituted 1-methylcyclohexene (entry 2). Acyclic 2-methyl-1-pentene affords 2-methyl-2-pentene in 85% yield (entry 3), with ca. 8% of starting material remaining. Allylbenzene is converted to the conjugated alkene in high yield (entry 4). Interestingly, butenylbenzene is predominately isomerized to the nonconjugated isomer, with only 6% overisomerization to the conjugated product (entry 5). Hepta-1,7-diene gives 40% conversion to doubly isomerized hepta-2,5-diene, with most of the residual material being the monoisomerization product (entry 6). Ketone-containing substrates are compatible with reaction conditions as well (entry 7). Isomerization of 5-bromo-1-pentene gives 64% of 5-bromo-2-pentene as a 1.9/1 trans/cis mixture (entry 8). Synthetically useful silyl-protected alcohols are also reactive. Triisopropylsilyl-protected pentenol is isomerized to the 2-isomer in 59% yield (entry 9). *t*-Butyldimethylsilyl protected methallyl alcohol affords isobutyraldehyde enol silane in 55% yield (entry 10). Protected allyl alcohol gives propionaldehyde enol silane in a good yield (entry 11). This reaction was repeated on a 20 mmol scale, and the product was isolated in 59% yield. The corresponding trimethylsilyl-protected alcohols did not give isomerization products, and free alcohols are unreactive.

Mechanistically, several possibilities can lead to selective formation of 2-olefins. The most likely scenario involves palladium migration along the alkyl chain by one carbon, β-hydride elimination, and internal olefin displacement (**4** to **7** to **8** to **9**, Scheme 1). This set of events was corroborated by

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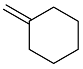
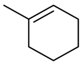
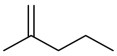
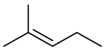
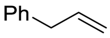
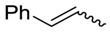
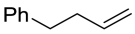
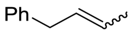
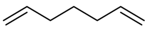
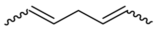
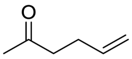
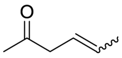
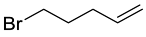
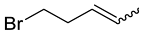
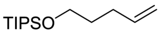
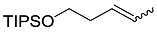
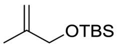
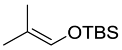
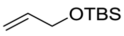
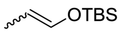
Table 1. Pd-Catalyzed Isomerization of Alkenes: Reaction Scope[a]

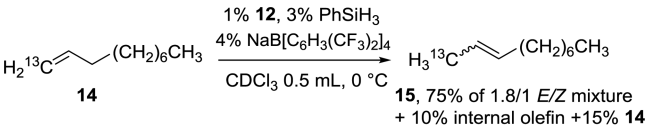
$$\underset{0.2\ \text{mmol}}{\text{1-Alkene}} \xrightarrow[\text{CDCl}_3\ 0.5\ \text{mL, } 0\ ^\circ\text{C}]{1\%\ \mathbf{12},\ 3\%\ \text{PhSiH}_3,\ 4\%\ \text{NaB}[\text{C}_6\text{H}_3(\text{CF}_3)_2]_4} \text{2-Alkene}$$

entry	alkene	product	yield, %
1[b]	1-Hexene	2-Hexenes	80 (2.1/1 E/Z)
2			94
3			85
4			93 (14.2/1 *E*/*Z*)
5[c]			78 (3.7/1 *E*/*Z*)
6[d]			40 (1.5/1 *EE*/*EZ*)
7[e]			91 (2.4/1 *E*/*Z*)
8			64 (1.9/1 *E*/*Z*)
9			59 (3.8/1 *E*/*Z*)
10			55
11			73 (3.5/1 *E*/*Z*); 59[f] (3.8/1 *E*/*Z*)

[a] Reactions were quenched by adding *t*BuNC. Yields were determined by ^{1}H NMR analysis against an internal standard. See the Supporting Information for details. [b] 3-Hexenes (7%) also formed. [c] Overisomerization product but-1-en-1-ylbenzene also formed (6%). [d] The remaining material is an isomeric mixture of hepta-1,5-dienes. [e] Overisomerization product 3-hexen-2-one also formed (4%). [f] Large-scale (20 mmol) reaction in CH_2Cl_2; isolated yield.

examining isomerization of 1-^{13}C-1-decene **14** (Scheme 4). After subjecting **14** to standard reaction conditions, 75% of 1-^{13}C-2-decene was obtained as a 1.8 *E*/*Z* isomer mixture, together with minor amounts of internal olefins and unreacted **14**. An alternative scenario that includes fast chain-running of palladium along the aliphatic chain, followed by a displacement of 2-olefin (in preference to terminal and 3-olefin), would result in about 1/1 mixture of 1-^{13}C-2-decene and 10-^{13}C-2-decene. Since the latter is not observed in the reaction mixture, this mechanistic pathway can be discounted.[6d]

Scheme 4. Isomerization of Labeled 1-Decene



In conclusion, we have shown that sterically hindered sandwich diimine-palladium complexes act as olefin isomerization catalysts. Terminal olefins are selectively converted to 2-olefins by a sequence of migratory insertion, *β*-hydride elimination, and olefin displacement reactions. The reaction tolerates functional groups such as ketones, silyl ethers, and halogens. The isomerization may be used to produce silyl enol ethers from protected allylic alcohols.

■ EXPERIMENTAL SECTION

General Procedure for Isomerization of 1-Olefins to 2-Olefins. A 2 dram vial with a screw cap (PTFE/Liner) equipped with a magnetic stir bar was charged with NaBArF (7 mg, 8 *μ*mol) and olefin (0.2 mmol). Freshly prepared solutions of catalyst **12** (5 mM in $CDCl_3$) and $PhSiH_3$ (60 mM in $CDCl_3$) were cooled to 0 °C. The precooled catalyst solution (0.4 mL, 2 *μ*mol) was added to the vial, followed by the addition of the precooled silane solution (0.1 mL of a 60 mM solution in $CDCl_3$, 6 *μ*mol) at 0 °C. Sequence of addition is crucial for obtaining high yields. The vial was sealed, placed in a cooling bath at 0 °C, and allowed to stir for the specified time. After the reaction had finished, *tert*-butyl isocyanide (approximately 6 *μ*L, >20 equiv to catalyst) was added, and the mixture was shaken to quench the reaction. The solution immediately turned from deep red to orange. An internal standard (1,4-bis(trifluoromethyl)benzene (7.8 *μ*L, 0.050 mmol) or pyridine (8.1 *μ*L, 0.010 mmol)) was added to the vial, and the whole reaction mixture was transferred to an NMR tube. Either the allylic $-CH_3$, allylic $-CH_2$, or olefin signal was used for quantification based on the best resolution in the spectra. Spectra were taken with a delay time of 20 s. The signal for *tert*-butyl isocyanide used to quench the reaction appears at 1.42 ppm.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00856.

Detailed experimental procedures and characterization data for new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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