Palladium Catalysis

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Activator-Free Olefin Oligomerization and Isomerization Reactions Catalyzed by an Air- and Water-Tolerant Wacker Oxidation Intermediate**

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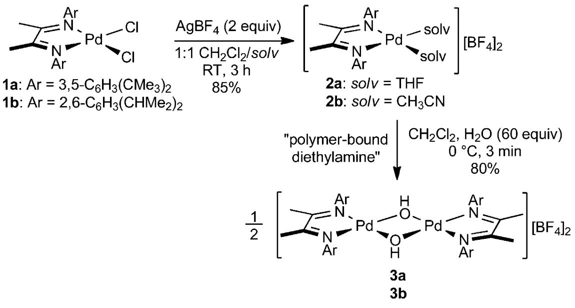
Olefin oligomerization is an important process that converts basic feedstocks, such as ethylene and propylene, into higher olefins used in the production of valuable products including linear low-density polyethylene, plasticizers, detergents, and lubricants.[1] Oligomerization (and polymerization) catalysis typically involves either a sensitive organometallic precursor or activators such as aluminum alkyls, and hence must be carried out under carefully controlled conditions, usually with exclusion of air and water.[2–4] Here we report that the bench-stable, hydroxy-bridged α-diimine-Pd dimer $[(\mathrm{ArN{=}C(Me)}-\mathrm{C(Me){=}NAr)Pd}(\mu\text{-OH})]_2^{2+}$ self-activates in the presence of substrate to a reactive, cationic Pd-hydride oligomerization and isomerization catalyst, allowing oligomerization and isomerization of olefins under air in wet solvent.

Synthesis of the hydroxy-bridged dipalladium dications, outlined in Scheme 1, requires only simple coordination complexes, rather than organopalladium precursors.[5] Addition of 1,4-bis(3′,5′-di-*tert*-butylphenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene ($^{t\mathrm{Bu}}\mathrm{DAB}_{\mathrm{Me}}$)[6] to $(\mathrm{PhCN})_2\mathrm{PdCl}_2$ generates complex **1a**. Ag$^{\mathrm{I}}$-promoted halide abstraction in THF affords bis(solvento) complex **2a**, which on treatment with water in the presence of a polymer-supported base ("polymer-bound diethylamine") gives precatalyst **3a** in approximately 70% overall yield from **1a**.



Scheme 1. Synthesis of dicationic bis(μ-hydroxy-bridged) Pd dimers.

In earlier studies of oxidative transformations under O_2 promoted by α-diimine-supported Pd complexes, bis(μ-hydroxy-bridged) dipalladium dications appeared to constitute thermodynamically stable "burial states" that would not exhibit further reactivity.[7] More recently we discovered that, under mild conditions, such complexes can effect certain stoichiometric C–H activations, including that of the allylic C–H bond in indene to yield an η^3-indenyl complex, and can catalyze the oxidative dehydrogenation of cyclohexene to benzene by O_2.[8] We expected that linear olefins would behave similarly, to produce η^3-allyl complexes and/or polyenes. Instead, in the presence of 0.1 mol% **3a** in a 2:1 $\mathrm{CH_2Cl_2}$/trifluoroethanol (TFE) solution, 1-hexene is almost entirely consumed within 40 min at room temperature by a combination of double-bond positional isomerization and oligomerization, to yield a thermodynamic distribution of linear hexenes as well as dimers, trimers, and tetramers (Figure 1). Similar behavior was observed with 1-pentene.[5] In both cases, after 7 h significant amounts of Pd black had precipitated and the catalyst was no longer active when more substrate was added.

Due to discrepancies in the literature, a discussion of the thermodynamic ratio of linear hexene isomers (Figure 1) is warranted. Previous reports have noted experimental distributions that differed substantially from thermochemically predicted values. A variety of explanations have been offered to come to terms with this inconsistency, some more plausible than others. However, none consider the simplest explanation—the published thermodynamic data, based on theoretical values derived using group additivity methods, or experimental ΔH_f values (from measured heats of hydrogenation or hydration) combined with theoretical entropies, may be imprecise and unreliable. Our experimental results and those from several published papers are shown in Table 1 and compared to predicted values. That the experimental data agree amongst themselves, yet have been obtained using a range of catalysts and solvents, strongly suggests that the experimental values, not the predicted ones, correctly reflect the thermodynamic equilibrium ratios, and that the error involved in calculating distributions based on theoretical thermochemical values is simply too large to predict this particular system's thermodynamic isomer distribution with any accuracy.

Isomerization proceeds faster than oligomerization, with turnover frequencies (TOF) of about 2100 h^{-1} and 200 h^{-1} at

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Supporting information for this article (experimental methods, isomer and oligomer analysis of reactions with **3a** and **7**, and crystallographic information for **8**) is available on the WWW under http://dx.doi.org/10.1002/anie.201206215.

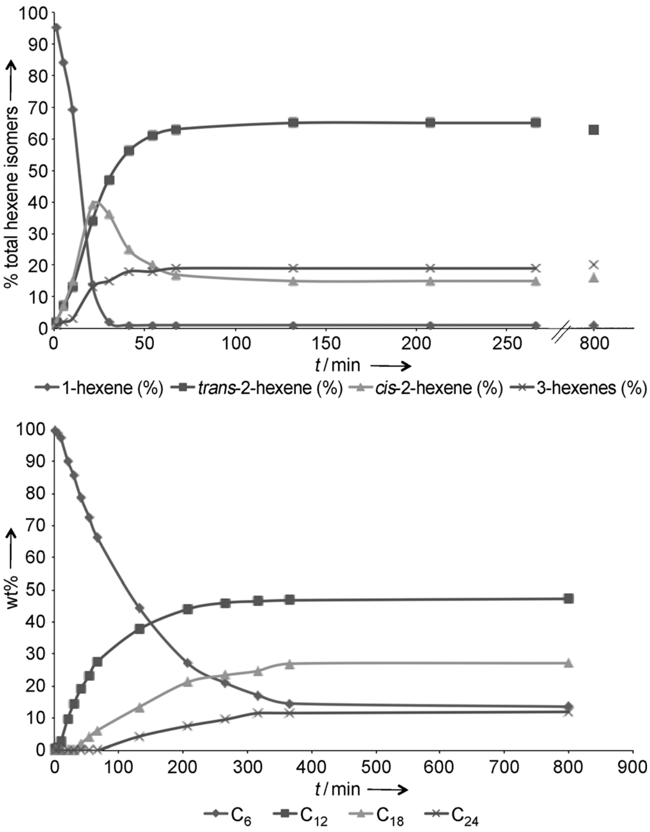


Figure 1. Isomerization (top) and oligomerization (bottom) of 1-hexene. Reaction conditions: 1-hexene (6.40 mmol), **3a** (0.1 mol%), CH_2Cl_2 (8 mL), TFE (4 mL), adamantane (internal GC standard), air, 25 °C.

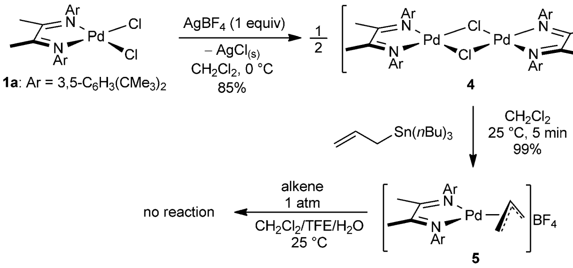
Table 1: Predicted and observed thermodynamic distribution of linear hexene isomers.[a]

1-Hexene	*trans*-2-Hexene	*cis*-2-Hexene	3-Hexenes	Ref.
		predicted		
0.4%	35.8%	39.0%	24.8%	[9]
0.3%	36.5%	38.9%	24.3%	[10]
1%	47%	20%	32%	[11]
1.0%	51.2%	15.2%	32.5%	[12]
		observed		
1%	64%	15%	20%	this work
1.2%	61.4%	16.6%	20.8%	[13]
1–3%	60–67%	14–19%	16–20%	[14]
1.6%	57.6%	16.2%	25%	[15]

[a] Reference (catalyst, solvent, temperature). This work (**3a**, CH_2Cl_2/TFE, 25 °C); Ref. [13] (Pd/Cu, MeOH, 25 °C); Ref. [14] (Ni/Al, $PhCH_3$, 25 °C); Ref. [15] ($[Fe_3(CO)_{12}]$, neat 1-hexene, 63 °C reflux).

25 °C, respectively. The isomerization/oligomerization catalyst obtained from **3a** appears to be quite insensitive to the presence of water or air, since the reaction rate and isomer/oligomer distributions remain essentially unchanged by addition of 2000 equivalents H_2O/Pd, or by running under 1 atm pure O_2. On the other hand, even though **3a** is stable in solution up to 100 °C, addition of olefin substrate at 40 °C results in significant catalyst decomposition to Pd black, suggesting that one or more post-activation species is temperature sensitive.

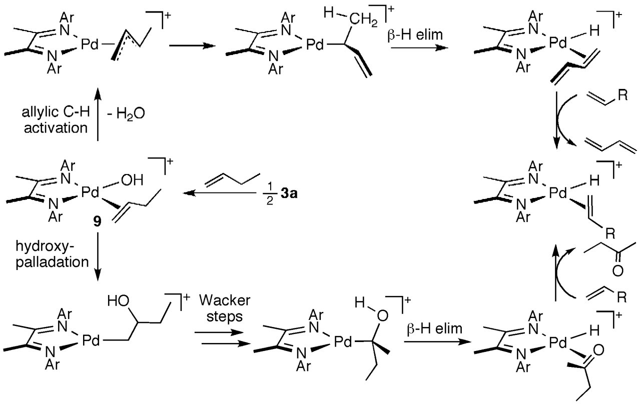
In light of the earlier findings, we noted that allylic C–H activation of alkene by **3a** with loss of water could conceivably initiate both isomerization and oligomerization by several possible mechanisms. However, two observations seem conclusively to rule out such mechanistic proposals involving initial allyl formation. First, ethylene, which obviously cannot undergo allylic activation, is readily oligomerized under similar conditions, with a TOF (at 1 atm at room temperature) of 600 h^{-1}. Propylene undergoes oligomerization at about the same rate; in both cases the products fit a Schulz–Flory distribution and consist primarily of branched isomers. Second, the intermediate that would result from allylic C–H bond activation of propylene, $[(^{tBu}DAB_{Me})Pd(\eta^3\text{-allyl})][BF_4]$ (**5**), could be independently prepared (Scheme 2) and was found *not* to catalyze either isomerization or oligomerization of alkenes under the standard reaction conditions.



Scheme 2. Synthesis of potential intermediate **5**.

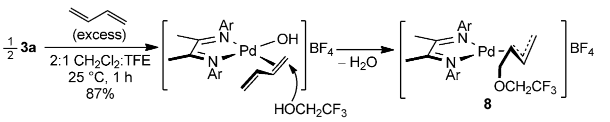
These observations suggest that catalysis proceeds through the more traditional mechanism involving insertion and β-hydride elimination, as proposed by Brookhart et al. for closely related Group 10 catalysts.[3] In support of this hypothesis, we found that $[(^{tBu}DAB_{Me})Pd(CH_3)(Et_2O)][BAr_4]$ (**7**; Ar = 3,5-$C_6H_3(CF_3)_2$), prepared in situ from $[(^{tBu}DAB_{Me})Pd(CH_3)_2]$ (**6**) and one equivalent of $[H(Et_2O)_2][BAr_4]$, converts 1-hexene with a rate and product distribution that are essentially equivalent to that obtained with **3a** as pre-catalyst.[5]

For a C_{4+} olefin, one route by which a putative hydride intermediate, required in the latter mechanism, could be generated from **3a** would be allylic C–H activation followed by β-hydride elimination. Such a sequence would generate a diene, and indeed very small amounts of hexadiene could be detected by gas chromatography following reaction of 1-hexene with **3a**. Unexpectedly, though, 2-hexanone (about five times as much) was also formed, with the total yield of those two products approximately equal to the original amount of Pd. The formation of stoichiometric amounts of ketone and diene implies that activation of **3a** by reaction with olefin involves two distinct pathways: the C–H activation/dehydrogenation sequence described above and a Wacker-like Pd-mediated oxidation (Scheme 3), with the latter somewhat faster.



Scheme 3. C–H bond activation and Wacker oxidation of olefin substrates (shown for 1-butene) to access a catalytically active Pd-hydride.

Stoichiometric formation of a C–O bond containing species was observed in the reaction of **3a** with 1,3-butadiene and weakly nucleophilic TFE under the same conditions, to afford 4-trifluoroethoxy-η^3-butenyl complex **8** (characterized crystallographically),[5] probably through attack of TFE at the terminal carbon of the η^2-bound diene [Eq. (1)]. The absence of trifluoroethyl enol ethers in the reactions with monoolefins suggests they begin with olefin insertion into the Pd–OH bond, followed by the standard Wacker sequence[16] to give ketone and the active Pd-hydride, as shown in Scheme 3.



(1)

The first steps of activation, leading to an intermediate such as **9** (Scheme 3), appear to require the presence of *both* olefin and TFE, as the NMR spectrum of dimer **3a** remains largely unchanged in neat TFE in the absence of olefins, while **3a** reacts with olefins only very slowly (on the order of days) in the absence of TFE. Perhaps coordination of both olefin and TFE to the Pd centers is required to facilitate dissociation of dimeric **3a**; indeed, Brookhart et al. have shown that ligand substitution in such tetracoordinate [(α-diimine)Pd] centers is an associative process.[3] As a consequence, complexes with bulky substituents at the *ortho*-positions of the aryl groups of the α-diimine ligand catalyze polymerization, rather than oligomerization; the axial face of the metal square plane is sterically blocked, inhibiting associative chain transfer relative to chain growth. We prepared a hydroxy-bridged dimer with such substituents, $[(^{iPr}DAB_{Me})Pd(OH)]_2(BF_4)_2$ (**3b**), in hopes of developing a self-activating polymerization catalyst. However, **3b** is completely inert and catalytically inactive, even at 80 °C under 1 atm ethylene; presumably the 2,6-isopropyl groups block the initial coordination of olefin and/or TFE needed to initiate catalyst activation.

There is a previous report of activator-free polymerization of ethylene by the related $[(^{iPr}DAB_{Me})Pd(MeCN)_2](BF_4)_2$ (**10**), but only at high pressures (20 atm), and with substantial inhibition by greater than trace amounts of water.[17] Here we are able to access a reactive Pd-hydride from an air- and water-stable precursor by simply adding olefin substrate, without the need for air- and/or water-sensitive catalysts and/or activators. Further studies on the scope of these oligomerization and isomerization reactions and the mechanism of catalyst activation, as well as extension to other catalyzed transformations, are continuing.

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