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General Catalyst Control of the Monoisomerization of 1-Alkenes to *trans*-2-Alkenes

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Supporting Information

ABSTRACT: After searching for the proper catalyst, the dual challenges of controlling the position of the double bond, and *cis*/*trans*-selectivity in isomerization of terminal alkenes to their 2-isomers are finally met in a general sense by mixtures of $(C_5Me_5)Ru$ complexes **1** and **3** featuring a bifunctional phosphine. Typically, catalyst loadings of 1 mol % of **1** and **3** can be employed for the production of (*E*)-2-alkenes at 40−70 °C. Catalyst comprising **1** and **3** avoids more than any other known example the thermodynamic equilibration of alkene isomers, as the *trans*-2-alkenes of both nonfunctionalized and functionalized alkenes are generated.

Alkenes are fundamental chemical feedstocks used on massive industrial scales.[1] and the alkene functional group is crucial to fine chemical synthesis, including multistep natural product synthesis.[2] The ability to control the formation and chemistry of alkenes is thus of central importance to organic synthesis in both industry and academia.

Alkene isomerization is deceptively simple, so it would seem that all synthetic problems in the area should be solved by now. However, one persistent issue is the simultaneous control of both regio- and stereochemistry, particularly in the case of converting a 1-alkene to a *trans*-2-alkene, without either forming the *cis*-2-alkene or isomerizing further down the chain. Though many catalysts succeed for functionalized or branched alkenes,[3] the challenge is especially acute (and unmet) when the alkene contains no branching or substituents of any kind to control overisomerization. What one would like is the same degree of control as that demanded and achieved routinely in asymmetric synthesis, where many reactions are optimized to exceed 90% ee, corresponding to a product ratio of >20:1.[4] As detailed in the next paragraph, for the most challenging case, that of unbranched alkenes or alkenes with remote branching, several alkene isomerization catalysts succeed at regiocontrol at the >20:1 level, but do not offer significant stereocontrol, giving *E*/*Z* ratios in the range of 2:5, which essentially amounts to only thermodynamic control by substrate. In contrast, here we report a general catalyst (a mixture of **1** and **3**, Figure 1), which at the 1 mol % level routinely offers both regio- and stereocontrol, with *E*/*Z* ratios >99 and product yields in excess of 95%.

As far as we are aware, *no other catalyst offers the same combination of regio- and stereocontrol as* ***1*** *+* ***3***; those that manage to achieve regiocontrol suffer from lack of stereocontrol, and in most cases are used at greater loadings or significantly higher

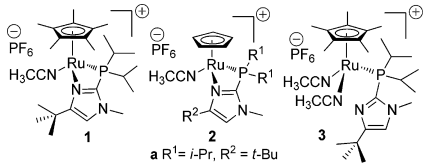

Figure 1. Bifunctional ruthenium catalysts for control of alkene isomerization.

temperatures. Focusing now on the more challenging linear hydrocarbon cases, we note that Veige's Cr(NCN)-pincer complex (10 mol %) offers some selectivity of 2-alkenes vs 3-alkenes (for hexene 95:5, octene 88:12) over 48 h at 85 °C; however, the product *cis*:*trans* ratios were not specified.[5a] Krompiec isomerized 1-hexene using $Ru(CO)_3(PPh_3)_2$ (0.5 mol %) to form 80% 2-hexene (*E*/*Z* = 2:1) and 16% 3-hexene in 3 h at 40 °C.[5b] Full conversion of 1-alkenes to 2-alkenes occurred using an unknown amount of $Ru_3(CO)_{12}$ as a catalyst, with the *cis*:*trans* ratio of product 2-octenes being 86:14.[5c] Very recently, Mo and co-workers have reported the isomerization of 1-octene to 2-octene (*E*/*Z* = 65:26), with small amounts of 3-and 4-octene, using a bulky Ir pincer complex (1 mol %) in 24 h at 150 °C, where NaOtBu was required as an additive.[5d] Beller et al. used $Fe_3(CO)_{12}$ (1 mol %) and 3 N KOH at 80 °C on 1-octene to make 96% 2-octene (*E*/*Z* = 3.1:1).[5e] A slightly higher selectivity for the *trans*-2-alkene was observed using $Fe(acac)_3$ (5 mol %) in 10 h at RT, where 50 mol % PhMgBr as additive was required, affording 97% 2-octene (*E*/*Z* = 5:1, essentially the thermodynamic *E*/*Z* ratio), in addition to 3-alkene and unreacted starting 1-octene.[5f] Thus, although several of these catalysts give high positional selectivity, none deviate significantly from the thermodynamic *E*/*Z* ratio of about 4:1, and generally suffer also from formation of the 3-alkene. The most selective protocol to date uses 50 °C and a Co-NHC complex (5 mol %) generated *in situ*, giving 81% 2-tetradecene (*E*/*Z* = 40:1) and 2% 3-alkene, in addition to 3% of 1-alkene.[5g] (*E*)-Selectivity makes these results stand well above from the rest, but a specialized Grignard reagent ($Me_2PhSiCH_2MgCl$, 50−100 mol %) needed to form the selective catalyst is incompatible with many functional groups; for example, a normal benzoic acid ester was not suitable, and 2-alkene selectivity was eroded in some cases by polar substituents.[5g]

Even our previously reported "alkene zipper" complex **2a**[6] does not generally solve the problem of simultaneous positional

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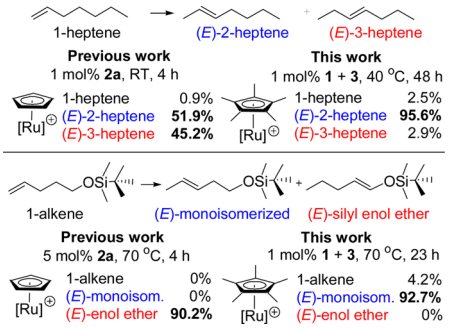
and geometric isomer control, as highlighted by comparisons in Scheme 1. With some branching or a certain functional group,

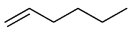
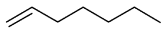
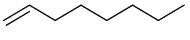
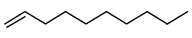
Scheme 1. Examples of Significant Differences between the Bifunctional $[Cp^*Ru]^+$ and $[CpRu]^+$ Complexes 1 + 3 and 2a



one can engineer the reaction conditions or substrate (e.g., by changing an alcohol protecting group) such that monoisomerization is achieved; *hence, catalyst control by* **2a** *is not complete.* In addition, by no means all branched substrates can be selectively monoisomerized. Thus, although **2a** is useful in many contexts,[6] the unsolved problem remains that **2a** is far too active for the monoisomerization of nonfunctionalized, simple hydrocarbon alkenes, like 1-heptene (Scheme 1), and the result is a mixture of *trans*-alkene isomer products. Most remarkably, the new catalyst comprised of **1** + **3** allows the selective monoisomerization of 1-heptene to *trans*-2-heptene in >95% yield, with <3% each of only two isomeric alkenes. To further highlight the distinct difference in reactivity, the *tert*-butyldimethylsilyl ether of pentenol is converted to exclusively the (*E*)-enol ether (3 bond movements, Scheme 1) with previously reported $[CpRu]^+$ derivative **2a**. In contrast, no enol ether is formed using the new $[Cp^*Ru]^+$ catalyst comprising **1** + **3**, and instead the (*E*)-monoisomerized product appears in >92% yield.

To achieve the new selectivity highlighted in Scheme 1, we hypothesized that we needed a catalyst with proper steric profile to discriminate between a 3-alkene and a 2-alkene using the slightly greater bulk of an ethyl substituent compared to that of a methyl substituent. First we tried increasing the steric bulk of the R^1 and R^2 groups of the phosphine ligand in **2** (Figure 1), but even at best, a mixture of internal isomers (*E*)-2- and 3-heptene was formed from 1-heptene.[6e] After considerable experimentation, we discovered a sufficiently selective catalyst (**1** + **3**) not by changing the phosphine ligand, but by modifying the ancilliary Cp ligand, eventually complexing $Cp^*Ru(CH_3CN)_3^+$ with the

Table 1. Control of Positional and Geometric Isomer Selectivity in Monoisomerization of Nonfunctionalized 1-Alkenes to the Corresponding (*E*)-2-Alkene Using Catalyst 1 (Entries 1–6) and Control Experiments (Entries 1a, 2a–2f)[a]

entry	reactant	catalyst	mol %	time	1-alkene remaining (%)	(*E*)-2-alkene yield (%)	(*E*)-3-alkene yield (%)	(*Z*)-2-alkene yield (%)
1		**1** + **3**	1	22 h	4.6	95.5	1.1[b]	<0.5[c]
				48 h	**2.3**	**95.5**	**2.1**[b]	**<0.5**[c]
1a		**2a**[d]	1	2 h	1.6	75.5	24.2	<0.5[e]
2		**1** + **3**	1	22 h	6.0	93.3	1.6	<0.5[c]
				48 h	**2.5**	**95.6**	**2.9**	**<0.5**[c]
2a		**2a**[d]	1	10 min	1.2	59.9	38.3	<0.5[e]
				4 h	0.9	51.9	45.2	<0.5[e]
2b		$RhCl_3/BH_3$[f]			0.7	43.3	36.0	12.7
2c		calculated[f]			0.5	59.7	39.8	0
2d		$Cp^*Ru(CH_3CN)_3^+ PF_6^-$[g]	2	66 h	81.8	8.5	4.2	2.0
2e		$Cp^*Ru(CH_3CN)_2(PiPr_3)^+ PF_6^-$	4	72 h[h]	97.9	0.7	<0.5	<0.5
2f		$Cp^*Ru(CH_3CN)_2(PiPr_2Ph)^+ PF_6^-$	4	72 h[h]	99.0	0.2	<0.5	<0.5
3		**1** + **3**	1	22 h	6.4	92.0	0.8	<0.5[c]
				48 h	**2.7**	**95.7**	**2.4**	**<0.5**[c]
4		(**1** + **3**) + CH_3CN	1	22 h	21.8	77.4	1.2	<0.5[c]
				48 h	6.2	91.8	1.1	<0.5[c]
				97 h	**2.7**	**94.7**	**2.7**	**<0.5**[c]
5		**3** + CH_3CN (catalyst made *in situ*)[i]	1	22 h	41.0	60.4	<0.5[e]	nd
				48 h	15.9	85.3	0.9	<0.5[c]
				97 h	**4.5**	**95.6**	**1.8**	**<0.5**[c]
6		**1** + **3**[j]	2	21 h	7.7	90.8	1.3	nd
				48 h	**2.6**	**95.8**	**2.2**	**nd**

[a]Acetone-d_6, 40 °C. Yields were determined by NMR integrations versus internal standard. Confirmatory alkene ratios were obtained using GC; please see Supporting Information (SI) for details. Less than a certain value means none detected, with the value given being estimated limit of detection. "nd" = not determined. [b](*E*)-3-Hexene best detected by NMR, because of overlap of GC peak with that of (*E*)-2-hexene. [c]Limit of detection using GC, comparison with authentic sample. [d]0.7 (entry 1a) or 1.0 mol % (entry 2a) **2a**, acetone-d_6, RT. [e]Limit of detection using NMR; no GC data at this time point. [f]Values from ref 7. Using $RhCl_3/BH_3$ (entry 2b), in addition, 7.3% (*Z*)-3-heptene formed. Entry 2c is based on heats of formation, and refers to values expected if only the three isomers 1-, (*E*)-2, and (*E*)-3-heptene could be formed. [g]Alkene % values are ratios analyzed by GC; a fifth peak, likely that of (*Z*)-3-heptene, 3.6%. [h]For data at earlier or later time points, and for detailed analysis leading to conclusion that **1** + **3** is >3000 times faster than the controls, see pages S38–S45 of SI. [i]Catalyst made *in situ* by mixing $Cp^*Ru(CH_3CN)_3^+ PF_6^-$ and phosphine ligand (1 mol % each), which gives bis(acetonitrile) complex **3** plus 1 equiv of free CH_3CN. [j]For data using 5 mol % **1** + **3** at RT, see SI; after 97 h, 93.3% (*E*)-2-decene and 5.7% 1-decene remaining.

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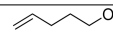
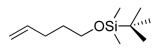
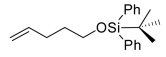
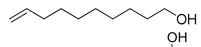
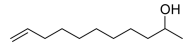
same ligand as in **2a**. The starting material Cp*Ru$(CH_3CN)_3^+$ isomerizes allylic alcohols to the corresponding carbonyl compound in refluxing CH_3CN,[8] but here in a control experiment (Table 1, entry 2d) we see that under conditions where **1** + **3** are very effective, Cp*Ru$(CH_3CN)_3^+$ PF_6^- only slowly consumes 1-heptene, giving a mixture of all isomers. Of even greater significance are control experiments (entries 2e and 2f) showing that *phosphine complexes without the pendant heterocycle are at least 3000 times slower than* ***1*** + ***3***,[9a] much like what we saw for **2a**.[6a]

The preparation and characterization of **1** deserve comment, in part because recent experiments point to the ability to use catalyst prepared *in situ*, and in part because the samples of **1** tested were all mixtures of **1** and *bis*(acetonitrile) species **3**. Adding phosphine to Cp*Ru$(CH_3CN)_3^+$ in a 1:1 molar ratio in acetone afforded a 1: 1 mixture of free CH_3CN and **3** within minutes. Removal of solvent left essentially pure **3**, with some chelate complex **1**. Adding fresh acetone and evaporating led to mixtures of **1** and **3**, typically in a ratio ranging from 1:5 to 1:2, which were used as catalyst to obtain the results in Tables 1 and 2.

Table 2. Monoisomerization of Functionalized 1-Alkenes to the Corresponding (*E*)-2-Alkenes Using Catalyst 1 + 3 (1 mol %)[a]

Entry	Reactant	Temp, °C	Time (h)	1-alkene remaining (%)	(*E*)-2-alkene yield (%)
1		40	5	16.9	81.7
			24	2.7	94.4
2a		40	23	14.3	85.2
			48	4.7	95.1
2b		70	5	5.8	92.2
			23	4.2	92.7
3[b]		40	23	8.2	87.9[c]
			48	5.0	90.2[c]
4		70	5	4.2	95.1[d]
5		40	23	6.3	93.4
			46	2.2	97.7

[a]Acetone-d_6. Yields from NMR integrations, see SI. [b]2 mol % with 6 mol % added ligand; see text. [c](*E*)-3-Alkene also seen (0.6 and 1.0% after 23 and 48 h), along with ∼1% of Cp*Ru-arene complex(es), likely of product. [d]3-Alkene (2.1%) also seen.

All attempts thus far to drive conversion of **3** to pure **1** were unsuccessful. Various NMR signals for **1** were broad no matter what temperature between +30 and −70 °C was used for observation, but at −20 °C, all ^1H and ^{13}C NMR resonances for **1** and **3** could be assigned using 1D and 2D NMR methods, except for the broadened peaks for the nuclei in the isopropyl groups on P. Hindered rotations caused by mutual steric hindrance of the Cp* methyls and phosphine iso-propyls may explain the broadened peaks. Notable is the one-bond coupling between P and the imidazole carbon directly attached, $^1J_{CP}$ = 58.0 Hz in **3** and 28.5 Hz in **1**, where from previous work[10] the sharply reduced coupling is diagnostic for the four-membered ring formed by a chelating imidazolylphosphine. Also, formation of the chelate engenders an upfield shift of the ^{31}P NMR resonance by 8.4 ppm.

Table 1 shows how the new [Cp*Ru]$^+$ catalyst comprised of **1** + **3** succeeds at controlled formation of *trans*-2-alkenes from linear hydrocarbon 1-alkenes, which as emphasized above are the greater challenge for catalyst control. Table 2 focuses on compounds that are functionalized but far from the alkene, thus offering little hope of steric or electronic control of isomerization. *In all cases, the generation of exclusively (E)-2-alkenes was observed.* Optimization of conditions performed on 1-octene, as detailed in SI, leads to final choice of conditions as 1 mol % **1** + **3** in acetone-d_6 solvent at 40 °C. Differences in rate of reaction or selectivity when either 1 or 2 mol % **1** + **3** is used are modest, but 5 mol % allows room temperature reactions (see footnote j of Table 1). Higher temperatures (e.g., 70 °C) were tested in an effort to speed reactions, but in general tended to cause some over-isomerization of substrates with challenging lack of hindrance to catalyst approach, such as the linear hydrocarbons in Table 1 or entries 2b and 4 of Table 2. Nitromethane gave rates comparable to those in acetone, but solubility was poorer, and CH_2Cl_2 gave slower reactions.

The optimum conditions for 1-octene were also applied to hexene, heptene, and decene (Table 1). NMR data were used to determine yields, and GC was used to confirm alkene ratios. Key ^1H and ^{13}C NMR resonances for *cis*- and *trans*-internal isomers are different enough to detect many of the components and determine yields. The (*E*)-2-alkene product dominated in all cases (ca. 95% yield) after 48 h. Looking at the 21 or 22 h data, and taking into account the use of 2 mol % catalyst for 1-decene, one discerns a slight decrease in rate on going from the smallest alkene to the largest, which may reflect greater steric hindrance from the longer alkyl chains. For all alkenes, less than 0.5% (detection limit) of (*Z*)-2-alkene was formed, but most significantly, no more than 3% of overisomerization ((*E*)-3-alkene) was seen. The small amount of 1-alkene remaining (2 to 3%) will never go away, because of thermodynamics; in a control experiment starting with pure (*E*)-2-heptene, after 22 h at 40 °C, 1-heptene (1.8%) was formed, showing equilibration. A small amount (1.0%) of (*E*)-3-heptene was also formed, even though (*E*)-2- and (*E*)-3-heptenes are almost equally stable.[7,9b]

The results described herein are notable, because of the calculated[7] thermodynamic distribution of heptene positional and geometrical isomers: 1-heptene (0.4%), (*E*)-2 (48.5%), (*Z*)-2 (11.7%), (*E*)-3 (32.4%), and (*Z*)-3-heptene (6.9%), values approached very closely in experiments using the $RhCl_3/BH_3$ catalyst system.[7] If only the terminal isomer and two internal *trans*-isomers are possible, as seen by values based on heats of formation in Table 1, entry 2c, the distribution of the three alkenes in the mixture would be 1-heptene (0.5%), (*E*)-2-heptene (59.7%), and (*E*)-3-heptene (39.8%), and these values are closely approached by our alkene zipper catalyst **2a** (entry 2a), confirming the accessibility of the less hindered CpRu derivative to the terminal alkene and all internal (*E*) isomers.

All attempts thus far to crystallize the mixture of **1** and **3** were unsuccessful. Our previously published catalyst **2a** was formed as a single species,[6a] but our experience with many potentially chelating phosphines[9c] shows that not all convert fully to chelates like **1** or **2a**, instead forming mixtures like those here. Given that ligand exchange on CpRu$(CH_3CN)_3^+$ is dissociative,[11] as we proposed for **2a**,[6a] presumably **1** and **3** both enter into alkene isomerization by loss of acetonitrile followed by alkene binding and allylic deprotonation.[6a,d] Therefore, we wanted to document the effects of nitrile amounts on isomerization rate, and also show conclusively that the positional selectivity of alkene isomerization by **1** + **3** is not caused by ca. 1.7 equiv of nitrile per Ru in the system (compared with reactions using pure **2a**, where the nitrile/Ru ratio is only 1:1). Thus, a control experiment using **1** + **3** and *added* CH_3CN (1 equiv) was performed. Table 1, entry 4, shows that adding 1 equiv of nitrile to **1** (+ **3**, giving nitrile: Ru ratio ca. 2.7 to 1) slows catalysis, but only by about 2-fold, giving the same excellent selectivity. Significantly, as seen from Table 1,

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entry 5, mixing Cp*Ru$(CH_3CN)_3^+PF_6^-$ and the requisite phosphine (1 mol % each) to afford **3** + CH_3CN (nitrile/Ru ratio 3:1) was just as effective, offering a convenient alternative. In summary, the precise ratio of **1** to **3** in the catalyst does not seem to affect rate or selectivity of isomerization, and **3** + CH_3CN formed *in situ* gives the same selectivity, with slightly reduced rate (~1/2) that seen using **1** + **3** mixtures.

Table 2 shows that compounds that are functionalized and protic can also be converted to (*E*)-2-alkenes with high selectivity using 1 mol % **1** + **3**. Pent-4-en-1-ol is easily transformed into >94% 3-penten-1-ol within 24 h (entry 1). The monoisomerization of 4-penten-1-ol with *cis*-Pt$(DMSO)_2Cl_2$ in water only gave 50% conversion to 3-penten-1-ol, after one day, with no mention of geometric selectivity.[12a] The corresponding silyl ether (entry 2) can be smoothly converted to the *trans*-monoisomerized product, without overisomerization at 40 °C and not until 23 h at 70 °C (2.5%). Lim et al. reported the promising monoisomerization of the hexenyl homologue of entry 2 with two multicomponent catalysts ((allyl)Pd or Ni halide dimer, phosphine, and AgOTf) in 80−95% yield but with *E*/*Z* ratios near 3.7:1,[12b] probably close to the thermodynamic values. Here, entries 4[13] and 5 show that longer chains bearing an alcohol at the remote end work equally well, neither being slowed nor suffering from reduced positional or geometric selectivity.

Initial experiments with aromatic reactants suggested that they were not well-tolerated by **1** + **3**, whereas they are by CpRu analog **2a**.[6-] The *tert*-butyldiphenylsilyl ether of pent-4-en-1-ol was transformed to the product of interest (29%) but catalyst deactivation occurred by liberation of the phosphine ligand and what appeared to be irreversible arene complex formation (as evidenced by loss of ^{31}P NMR peaks for **1** and **3**, appearance of a peak for free phosphine, and appearance of ^1H resonances between 5.9 and 6.2 ppm tentatively assigned to metalated arene). Perhaps because of release of steric strain, dissociative phosphine loss from **1** and **3** is more pronounced than from **2a**. We note that phosphine-free species Cp*Ru$(CH_3CN)_3^+$ PF_6^- is a poor catalyst (Table 1, entry 2d), so the activity and high selectivity exhibited by **1** + **3** requires the phosphine. Importantly, solving the arene binding problem is possible. The successful result of Table 2, entry 3, was achieved with 2 mol % **1** + **3** and added bifunctional imidazolylphosphine ligand (6 mol %), which suppressed Cp*Ru-arene complex formation enough to allow for >90% yield of monoisomerized product to form.

In summary, we show that a new Cp*Ru^+ catalyst comprising **1** + **3** offers unparalleled *catalyst* control of both position and geometry in the isomerization of 1-alkenes to (*E*)-2-alkenes, with product yields typically about 95% even when polar substituents are present. Protic and carbonyl (acetone solvent) functional groups are tolerated; neither strong base, nucleophile, nor acid is present. The preformed catalyst and **3** formed conveniently *in situ* show the same high catalyst control. Both the Cp* and bifunctional ligands are absolutely essential for activity and selectivity. The results here are part of an ongoing program to build a toolbox of catalysts and chemistry for selective alkene transformation, and further reports will appear in due course.

■ ASSOCIATED CONTENT

Supporting Information

Details of catalyst preparation, spectra, characterization and catalysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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