Z-Selective Alkene Isomerization by High-Spin Cobalt(II) Complexes

Chi Chen,[†,‡] Thomas R. Dugan,[†] William W. Brennessel,[†] Daniel J. Weix,*[,†] and Patrick L. Holland*[,†,‡]

[†]Department of Chemistry, University of Rochester, 120 Trustee Road, Rochester, New York 14627, United States
[‡]Department of Chemistry, Yale University, 225 Prospect Street, New Haven, Connecticut 06520, United States

S *Supporting Information*

ABSTRACT: The isomerization of simple terminal alkenes to internal isomers with Z-stereochemistry is rare, because the more stable E-isomers are typically formed. We show here that cobalt(II) catalysts supported by bulky β-diketiminate ligands have the appropriate kinetic selectivity to catalyze the isomerization of some simple 1-alkenes specifically to the 2-alkene as the less stable Z-isomer. The catalysis proceeds via an "alkyl" mechanism, with a three-coordinate cobalt(II) alkyl complex as the resting state. β-Hydride elimination and [1,2]-insertion steps are both rapid, as shown by isotopic labeling experiments. A steric model explains the selectivity through a square-planar geometry at cobalt(II) in the transition state for β-hydride elimination. The catalyst works not only with simple alkenes, but also with homoallyl silanes, ketals, and silyl ethers. Isolation of cobalt(I) or cobalt(II) products from reactions with poor substrates suggests that the key catalyst decomposition pathways are bimolecular, and lowering the catalyst concentration often improves the selectivity. In addition to a potentially useful, selective transformation, these studies provide a mechanistic understanding for catalytic alkene isomerization by high-spin cobalt complexes, and demonstrate the effectiveness of steric bulk in controlling the stereoselectivity of alkene formation.
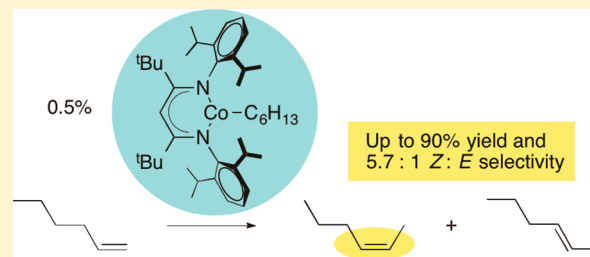
INTRODUCTION

Alkenes are key functional groups in many natural and industrial products, as well as precursors for other types of organic molecules. Among the methods available for the formation of alkenes, relatively few allow direct access to the thermodynamically less-stable Z-isomer, even though Z-alkenes are of great use in synthesis and are commonly found in natural products.[1] Common ways to access Z-alkenes include the Wittig olefination,[2,3] the Still–Gennari modification to the Horner–Wadsworth–Emmons olefination,[4] the cross-coupling of Z-vinyl halides or Z-vinyl organometallic reagents,[5] reduction of alkynes over a poisoned catalyst,[6] and, recently, Z-selective olefin metathesis.[7–9] An approach that has not yet met with great success is selective alkene isomerization (Figure 1),[10,11] even though isomerization is an atom-economic organic transformation that has many applications in industry.[11]
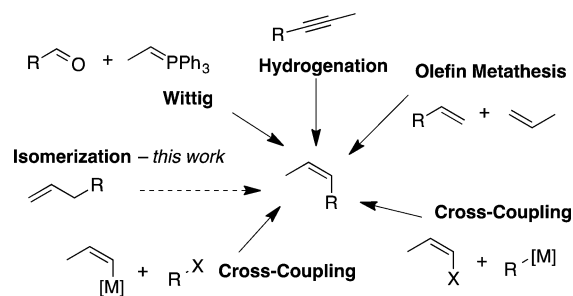
Although the isomerization of terminal alkenes to internal alkenes is thermodynamically favorable, catalytic reactions often give mixtures of internal alkenes.[12–24] Further, the products are typically mixtures of the E- and Z-isomers in the ratio expected from the relative free energies (for simple alkenes, this ratio is generally greater than 3:1 favoring the E-isomer).[12,25–28] Several catalysts are known for selective formation of the E-isomer with very good selectivity.[14,17,18,29–31] On the other hand, *selectivity for the less thermodynamically stable internal isomer is rare.* Some alkene isomerization catalysts form the Z-isomers at a very early stage, but the mixture quickly converges to the predominantly E thermodynamic ratio.[32] One successful strategy for overcoming thermodynamically dominated selectivity has been to use a directing group, for example in the isomerization of 2-allylphenol to its Z-2-isomer with Ru(cot)(cod)/PEt₃,[33] and the isomerization of 1,3-dienes to 2Z,4E-dienes with CoBr₂(dpppMe₂).[34] A few homogeneous catalysts selectively produce the E-isomer of vinyl ethers, amines, and acetates, which is the less stable isomer.[14,30,35–37] However, selectivity for the less-stable Z-isomer of simple olefins remains an unsolved challenge. We report here the selective isomerization of normal α-olefins to Z-2-olefins through the action of a sterically demanding cobalt(II) catalyst.

The mechanisms of metal-catalyzed alkene isomerizations have been studied in great detail.[38] The two most common mechanisms are termed alkyl and allyl mechanisms (Scheme 1). In the alkyl mechanism (Scheme 1a), sequential β-hydride

Figure 1. Approaches to Z-olefins.

Scheme 1. Mechanisms of Catalytic Alkene Isomerization

(a) alkyl mechanism
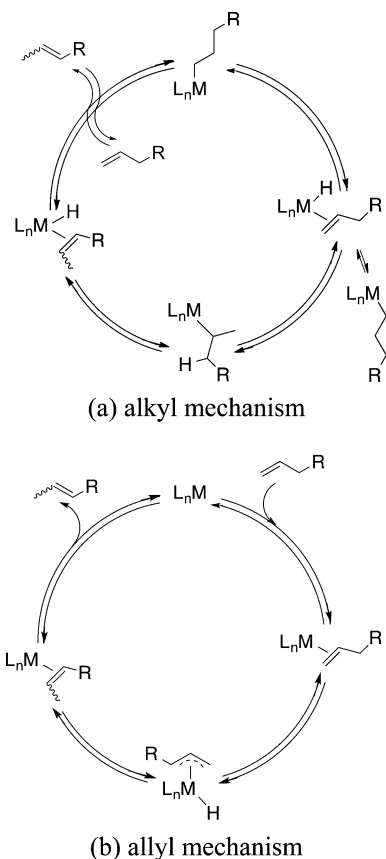
(b) allyl mechanism

elimination and [1,2]-insertion cause migration of the metal, and the oxidation state of the metal is constant. In contrast, the allyl mechanism (Scheme 1b) involves the reversible oxidative addition of allylic C−H bonds.

In this work, we describe the isomerization of alkenes using a paramagnetic cobalt(II) catalyst that has a high-spin electronic configuration. High-spin paramagnetic complexes present challenges for study, because these complexes do not follow the "18-electron rule," and the NMR spectra of the complexes contain broadened and shifted resonances. Despite these issues, a number of groups have discovered interesting and distinctive reactivity from high-spin complexes.[39,40] In a relevant example, we have shown that three-coordinate β-diketiminate iron(II) alkyl complexes perform reversible β-H elimination followed by alkene exchange, which results in transfer hydrogenation and/or isomerization of alkyl ligands.[41,42] These transformations comprise the first two steps of the alkyl mechanism for alkene isomerization, but preliminary investigations indicated that the iron(II) complexes were very slow isomerization catalysts.

We have also reported three-coordinate cobalt(II) alkyl complexes $L^{tBu}CoR$ (R = methyl, cyclohexyl) supported by the bulky ligand 2,2,6,6-tetramethyl-3,5-bis(2,6-diisopropylphenylimido)heptyl (L^{tBu}, see Figure 2).[43−45] These complexes were characterized by a range of structural and spectroscopic techniques, showing that they have a high-spin d^7 ($S = ^3/_2$) electronic configuration. Here, we report that the related complex $L^{tBu}Co(n\text{-hexyl})$ mediates efficient alkene isomerization through an alkyl mechanism, and we evaluate the scope and mechanism of the reaction as well as mechanisms of catalyst decomposition. These studies are important because
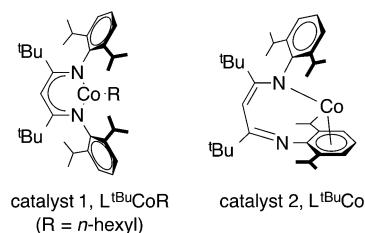

Figure 2. Catalysts used in this study. The cobalt(II) catalyst **1** is an effective and selective catalyst that shows the hallmarks of a homogeneous catalyst.

they show exceptional selectivity: they are selective for 2-alkenes, and specifically form the Z-isomer.

■ RESULTS

Synthesis and Characterization of Catalysts. As previously reported, β-diketiminate-supported cobalt(II) alkyl complexes can be synthesized by reacting $L^{tBu}CoCl^{46}$ with Grignard reagents.[43,44] In order to provide a suitable catalyst with β-hydrogen atoms on the alkyl ligand, we prepared $L^{tBu}Co(n\text{-hexyl})$ (**1**) from the corresponding Grignard reagent. This compound is extremely sensitive to air and to moisture, and its characterization and catalytic reactions were studied under rigorously dry conditions under argon or N_2. The molecular structure of **1** was determined by X-ray crystallography (Figure 3). The Co−N bond distances and the N−Co−
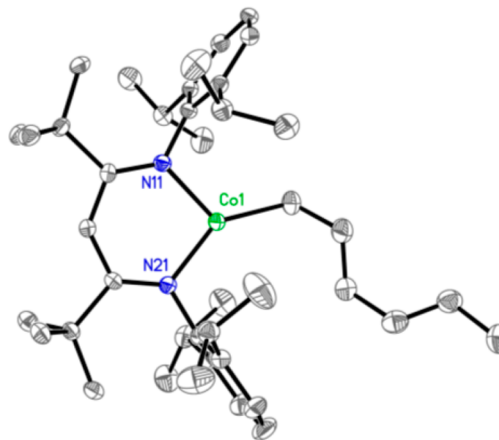

Figure 3. ORTEP drawing of the molecular structure of **1**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Important bond distances (Å) and angles (deg): Co−N 1.950(2), 1.960(2), Co−C 2.011(2); N−Co−N 97.69(7), N−Co−C 120.60(9), 141.26(9).

N angle are similar to those in planar three-coordinate β-diketiminate cobalt(II) complexes like $L^{tBu}CoCl$ and $L^{tBu}CoCH_3$.[43] The Co−C bond distance of 2.011(2) Å is longer than that in $L^{tBu}CoCH_3$ (1.963(3) Å), probably due to the added steric hindrance. The ^1H NMR spectrum of **1** shows resonances that are paramagnetically shifted and lie over a range of more than 300 ppm. Resonances in the β-diketiminate ligand can be assigned on the basis of integration to the seven unique proton environments, with chemical shifts similar to those of $L^{tBu}CoCH_3$.[43] Therefore, the solution symmetry is C_{2v}, indicating that rotation around the Co−C bond is rapid on the NMR time scale. Additionally, resonances corresponding to

protons of the hexyl ligand were evident, corresponding to all except the two closest to the paramagnetic cobalt(II) center.

Catalysis was also tested using a previously reported high-spin cobalt(I) complex L^{tBu}Co (**2**), in which the supporting β-diketiminate ligand has κ^1:η^6-binding to the metal (Figure 2).[47] Despite the unusual binding mode, this complex is known to react through pathways that rearrange the supporting ligand back to the traditional κ^2 binding, with coordination of additional donors.

Isomerization of 1-Alkenes to 2-Alkenes. We began with isomerization of 1-hexene to 2-hexene in benzene solution, with mesitylene as an internal standard for gas chromatography (GC) (Scheme 2). Initial reactions used 1 M 1-hexene and 1%

Scheme 2. Cobalt-Catalyzed Isomerization of 1-Hexene
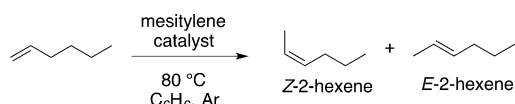
loading of cobalt catalyst at 80 °C for 24 h, and the progress of the reactions was monitored by GC and verified by ^{1}H NMR spectroscopy. Both catalysts gave regioselective isomerization to 2-hexenes, and <5% of 3-hexenes were observed. Therefore, the isomerization does not reach thermodynamic equilibrium.

Interestingly, the selectivity is very different for the two catalysts (Table 1). Catalysis by **2** gives E:Z ratios near the

Table 1. Isomerization of 1-Hexene to E- and Z-2-Hexenes with 1 and 2[a]

catalyst	time (h)	yield[b]	E:Z[b]
1	6	63%	1:6.9
1	12	88%	1:4.2
1	24	88%	1:2.5
2	6	36%	4.1:1
2	12	50%	4.0:1
2	24	62%	3.8:1

[a]1.0 mol % catalyst loading, 80 °C, 1.0 M substrate. [b]Yields of products and E:Z ratios were determined by GC analysis.

thermodynamic ratio of 4:1.[48] When a drop of elemental mercury was added to the isomerization reaction catalyzed by **2**, the rate of isomerization decreased significantly. The mercury effect strongly implicates a heterogeneous Co colloid as the actual catalyst, which would be generated from degradation of **2**.

On the other hand, catalysis by **1** gave impressive selectivity for the less thermodynamically preferred Z-2-isomer at early times, and the selectivity slowly degraded at later times (see below for more detail). The reaction rate and the selectivity of isomerization catalyzed by **1** were unchanged by the addition of mercury, suggesting that it remains a homogeneous catalyst under the reaction conditions.[49] Therefore, *all subsequent studies were performed with catalyst 1*.

The unusual Z-selectivity of catalyst **1** was dependent on the solvent, temperature, catalyst loading, and substrate concentration. Tables 2 and 3 show the results obtained when stopping the reaction after 12 h, a time period that was a good balance between conversion (which increased over time) and selectivity (which began to degrade at longer times).

The Z-selectivity was enhanced in aromatic solvents (entries 1–4 in Table 2). The reaction rate was faster at higher

Table 2. Solvent Dependence of 1-Hexene Isomerization with Catalyst 1[a]

entry	solvent	yield[b]	E:Z[b]
1	benzene	88%	1:3.9
2	toluene	83%	1:3.2
3	THF	84%	1:2.1
4	nonane	86%	1:0.9

[a]Reaction conditions: 1 equiv mesitylene, 0.5 mol % catalyst, 80 °C, 12 h. [b]Yield of products and E:Z ratios determined by GC analysis.

Table 3. Variation of Conditions for Isomerization of 1-Hexene with Catalyst 1[a]

entry	T (°C)	catalyst loading (mol %)	[1-hexene] (mol/L)	yield[b]	E:Z[b]
1	25	0.5	1.0	6%	all Z
2	45	0.5	1.0	11%	1:4.9
3	60	0.5	1.0	31%	1:5.7
4	80	0.5	1.0	88%	1:5.3
5	80	1.0	1.0	86%	1:2.8
6	80	5.0	1.0	90%	1:0.3
7	80	0.5	0.1	47%	1:5.7
8	80	0.5	0.5	72%	1:5.6
9[c]	80	0.5	1.0	86%	1:4.5
10[d]	80	0.5	1.0	84%	1:4.0

[a]The reaction solvent is benzene, and the reaction time is 12 h unless otherwise specified. [b]Yield of products and E:Z ratios determined by GC analysis. [c]Added 2 drops of Hg. [d]Added 0.025 mol % PPh$_3$.

temperature, but temperature did not have a significant impact on the selectivity up to 80 °C (entries 1−4 in Table 3). The catalyst loading had a significant influence on the Z-selectivity, with higher selectivity at lower loading (entries 4, 5, and 6 in Table 3). The concentration of substrate did not affect selectivity and reactivity significantly (entries 4, 7, and 8 in Table 3).

Scope: Aliphatic and Aromatic Alkenes. To investigate the scope of the isomerization reaction catalyzed by L^{tBu}Co(n-hexyl), we tested other terminal alkenes.

The cobalt-catalyzed isomerization reaction as shown above was effective for aliphatic alkenes, even for substrates that form a bulky trisubstituted alkene products. 1-Octene and 1-dodecene give even better discrimination between E- and Z-products, but gave products from more extensive isomerization of the double bond to other internal positions. The yields for these substrates in Table 4 reflect only the 2-isomers; other internal isomers could not be distinguished from one another by ^{1}H NMR spectroscopy, including their E:Z ratios. Since these alkenes reacted more quickly, the amount of over-isomerization could be minimized by shortening the reaction time, at minor expense to the conversion (Table 5).

Homoallylsilane could be isomerized to Z-crotylsilane with high selectivity, showing the tolerance of the reaction to silanes. However, isomerization of allylsilanes to vinylsilanes gave more E- than Z-product (Table 4, entries 7 and 8). This loss of Z-selectivity is attributed to formation of a heterogeneous catalyst, because the reactivity of allylsilanes decreases significantly upon addition of a drop of Hg (the Z-selective conversion of homoallylsilane remains unaffected). The same phenomenon was observed with dienes: 4,8-dimethylnona-1,7-diene (Table 4, entry 6) gave isomerization of terminal double bonds to mostly E-product, but activity decreases with addition of Hg. Thus, under conditions we examined, the homogeneous

Table 4. Isomerization of Other Alkenes[a]

Entry	Starting material	Major Product	Time (h)	Yield[b]	E:Z[b]	S.M Remaining[b]
1[c]	(structure)	(structure)	12	67%[d]	1:7.2	3%
2[c]	(structure)	(structure)	12	38%[d]	1:6.3	2%
3	(structure)	(structure)	12	89%[e]	N/A	2%
4	(structure)	(structure)	24	92%	ND	<1%
5	(structure)	(structure)	48	84%	N/A	<1%
6	(structure)	(structure)	18	94%	3:1	3%
7[f]	(structure)	(structure)	16	74%	10:1	25%
8	(structure)	(structure)	16	61%	6.6:1	25%
9[f]	(structure)	(structure)	12	87%[g]	1:9.1	5%
10	(structure)	(structure)	12	83%[h]	1:5.6	5%
11[i]	(structure)	(structure)	24	90%	1:6.0	3%
12	(structure)	(structure)	24	20%	1:0.4	77%
13	(structure)	(structure)	24	37%	1:0.2	54%
14	(structure)	(structure)	24	25%[j]	1:0.4	70%
15	(structure)	(structure)	24	58%[k]	1:1.9	41%

[a] 5 mol % catalyst, 80 °C. [b] Yield and E:Z ratio determined by NMR analysis. N/A = not applicable; ND = E,Z-mixture could not be resolved. [c] 0.5 mol % catalyst, 80 °C. [d] Other internal products observed; see Table 5 for details. [e] 5% of 1-ethylcyclohexene. [f] 2 mol % catalyst, 80 °C. [g] 7% of but-1-en-1-yl trimethylsilane. [h] 9% of tert-butyldimethyl((2-methylpent-2-en-1-yl)oxy)silane. [i] 1 mol % catalyst, 80 °C. [j] 3% of but-1-en-1-ylbenzene. [k] Trace amount of pent-1-en-1-ylbenzene observed.

Table 5. Isomerization from 1-Octene and 1-Dodecene at Different Reaction Times[a]

	reaction time (h)	conversion	2-alkene	E:Z for 2-alkene	other internal alkenes
1-octene	12	93%	67%	1:7.2	26%
1-octene	8	89%	68%	1:10	21%
1-dodecene	12	95%	37%	1:5.3	58%
1-dodecene	7	89%	58%	1:6.3	31%

[a] 0.5 mol % catalyst loading, 80 °C; yields and E:Z ratios determined by ^{1}H NMR spectroscopy.

catalyst always displayed Z-selectivity, but degradation of the selective catalyst by certain substrates gave products near the thermodynamic ratio.

The cobalt-catalyzed alkene isomerization also tolerated silyl-protected alcohols with branched methyl, protected ketone, and aromatic alkenes. Alkenes containing an aromatic ring gave low conversion and poor Z-selectivity under standard conditions, but it was possible to improve these isomerizations through manipulation of conditions (discussed below). Terminal dienes (1,5-hexadiene and 1,7-octadiene) gave no isomerization products, and the catalyst decomposed. Alcohols rapidly degraded the catalyst; some silyl-protected alcohols (silyl ethers) also reacted with the catalyst, through a reaction that will be discussed in more detail below. However, the presence of a methyl substituent between the terminal alkene and the siloxy group was sufficient to enable TBS-protected alcohols to give excellent yields of Z-2-isomers under standard reaction conditions, with no impact on the siloxy group.

In an effort to explain the poor performance of aromatic alkenes and dienes, we isolated decomposition products from the attempted isomerizations of allylbenzene and 1,5-hexadiene, and characterized them using X-ray crystallography.

The X-ray crystal structure of the product from the reaction of 1 with allylbenzene (Figure 4) shows η^2-allylbenzene coordinated to a cobalt(I) complex. The Co−N bond distances in $L^{tBu}Co(\eta^2$-allylbenzene) are similar to Co−N bond distances in other $L^{tBu}Co^I$ complexes.[47] The C=C bond is neither in the diketiminate plane nor perpendicular to it, as observed in the iron complex $L^{Me}Fe(\eta^2$-styrene).[50] The C=C bond distance is elongated from 1.34 Å in a typical alkene[51] to 1.382(3) Å by coordination to cobalt(I). This coordinated C=C bond is not as long as those in $L^{Me}Fe(\eta^2$-styrene) (1.401(8) Å)[50] and $L^{Me}Fe(Ph_2C=CH_2)$ (1.411 Å),[50,52] probably because of reduced backbonding from the more electronegative cobalt. The C=C−C angle of 122(2)° is slightly larger than the expected 120° for sp^2-hybridized carbon, presumably from steric effects.

This cobalt(I) complex was synthesized independently by mixing allylbenzene with $L^{tBu}Co$, and was fully characterized. It is high-spin (S = 1) and paramagnetic, but has a relatively sharp,
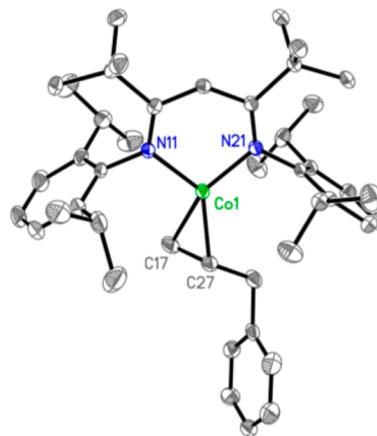

Figure 4. ORTEP drawing of $L^{tBu}Co(\eta^2$-allylbenzene), which came from attempted isomerization of allylbenzene by catalyst 1. Thermal ellipsoids shown at the 50% probability level. Hydrogen atoms omitted for clarity. Important bond distances (Å) and angles (deg): Co−N 1.9386(16), 1.9849(16), Co−C 2.027(2), 2.034(2), C−C 1.382(3); N−Co−N 96.47(7).

well-resolved ^{1}H NMR spectrum. The coordinated alkene causes a reduction of symmetry from C_{2v} to C_2, which is reflected in the larger number of peaks observed in the NMR spectrum (see Experimental Section). The ^{1}H NMR spectrum of $L^{tBu}Co(\eta^2\text{-allylbenzene})$ matched the paramagnetic part of the spectrum for mixtures generated from the catalytic isomerization of allylbenzene.

An attempted diene isomerization reaction also yielded a crystal suitable for X-ray crystallography. The crystal structure showed a dicobalt(I) hexadiene complex with the two C=C bonds of 1,5-hexadiene coordinated to two different cobalt centers (Figure 5). The C=C bond is neither in the β-
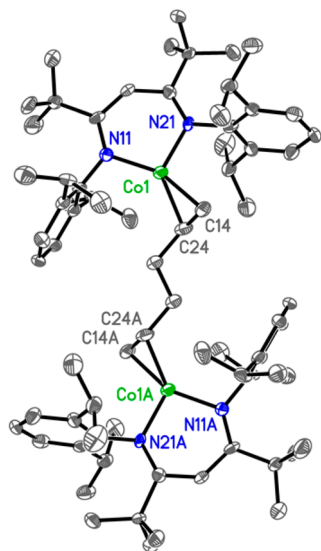

Figure 5. ORTEP drawing of the molecular structure of $(L^{tBu}Co)_2(\mu\text{-}\eta^2{:}\eta^2\text{-1,5-hexadiene})$. Thermal ellipsoids at 50% probability. Hydrogen atoms omitted for clarity. Important bond distances (Å): Co−N 1.974(5), 1.950(5); N−Co−N 96.9(2).

diketiminate plane nor perpendicular to it, which is similar to $L^{tBu}Co(\eta^2\text{-allylbenzene})$ and $L^{Me}Fe(\eta^2\text{-styrene})$.[50] The molecule lies on a crystallographic inversion center; thus, one-half is unique. The two β-diketiminate planes are parallel to each other, and the two C=C bonds are parallel. The C=C bond distances are elongated from 1.34 Å in a typical alkene[51] to 1.394(9) Å, which is similar to that in $L^{tBu}Co(\eta^2\text{-allylbenzene})$. As in $L^{tBu}Co(\eta^2\text{-allylbenzene})$, the C=C—C angle (125.3(7)°) is larger than expected for a sp^2 hybridized carbon.

The isolation of these two products suggests that the active cobalt(II) catalyst can be reduced to unselective or inactive cobalt(I) species in the presence of certain substrates. In the case of allylbenzene, mechanistic insight came from the fact that propylbenzene was detected in the final reaction mixture by GC−MS. To explain the transformation from $L^{tBu}Co(n\text{-hexyl})$ to $L^{tBu}Co(\text{alkene})$, we propose a tentative mechanism consisting of a bimolecular hydrogen atom transfer followed by reductive elimination of a C−H bond (Scheme 3). In the disproportionation, we cannot rule out the involvement of free radicals, but a pathway with intermolecular hydrogen atom transfer directly between cobalt centers has more precedents in intermolecular hydrogen atom transfer reactions from metal hydrides.[53−58] Because this reaction involves two cobalt species reacting with one another, it predicts that lowering the concentration of catalyst should lower the rate of the bimolecular reaction and therefore prevent catalyst decom-

Scheme 3. Proposed Bimolecular Mechanism of Catalyst Decomposition with Aromatic Substrates
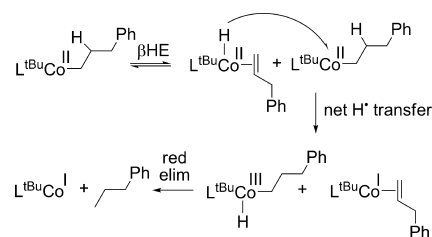
position. Consistent with this hypothesis, lowering the substrate and catalyst concentrations by a factor of 20 gave much better conversion and selectivity (Table 6).

Table 6. Allylbenzene Isomerization with Different Catalyst Concentrations[a]

entry	[cat.] (mM)	yield[b]	E:Z[b]	starting material recovered[b]
1	50.0	17%	1:0.4	77%
2	25.0	24%	1:0.6	65%
3	5.0	44%	1:1.3	50%
4	2.5	90%	1:1.4	trace

[a]5 mol % catalyst, 80 °C. [b]Yields and E:Z are determined by NMR analysis.

Using the modified substrate concentration of 0.05 M, the isomerization of aromatic substrates gave significantly better results (Table 7).

Table 7. Isomerization of Aromatic Substrates at Lower Concentration[a]

Entry	Starting material	Major Product	Yield[b]	S.M.[b] recovered	E:Z[b]
1			40 h, 90%	Trace	1:1.4
2			40 h, 73%	18%	1:1.4
3			40 h, 65%[c]	11%	1:12
4			40 h, 89%[d]	7%	1:6.1

[a]0.05 M substrate, 5 mol % catalyst, 80 °C. [b]Yields and E:Z determined by NMR analysis. [c]13% but-1-en-1-ylbenzene observed (E:Z = 1: 1). [d]10% of pent-1-en-1-ylbenzene observed (E:Z = 1:1.1).

All isomerizations of aromatic substrates are Z-selective, though the selectivity is lower for the formation of styrene derivatives. Using substrates for which migration by a single double bond to an allylic or homoallylic product was desired, NMR spectra showed small amounts of styrene derivatives formed from more extensive isomerization.

The mechanism through which dienes degrade the catalyst is unknown. Interestingly, dilution of the reactions gives no improvement in the diene reaction, which suggests that the decomposition of catalyst proceeds through a different mechanism than that described for the aromatic substrates above.

Mechanistic Studies: Cobalt Profile. The cobalt species present in the catalytic mixture during the isomerization reaction could be monitored by ^{1}H NMR spectroscopy. These studies benefit from the paramagnetic shifts in the proton NMR resonances of the cobalt complexes, which are easily distinguished from those of diamagnetic substrates and products. During the reaction, the only cobalt species observed is L^{tBu}Co(*n*-hexyl). When L^{tBu}CoEt is used as an alternative precatalyst for 1-hexene isomerization, L^{tBu}Co(*n*-hexyl) is still observed as the paramagnetic cobalt species. This observation indicates that the cobalt–alkyl complex is the resting state for the catalytic cycle, and that alkene exchange is facile.

We assume that other L^{tBu}Co(alkyl) complexes are present in low concentrations during catalysis; however, they must be thermodynamically less stable and rearrange rapidly to L^{tBu}Co(*n*-hexyl). We tested this idea by treating L^{tBu}CoCl with 3-hexylmagnesium bromide at room temperature, which immediately gave the isomerized product L^{tBu}Co(*n*-hexyl). This experiment shows that the terminal alkyl isomer is more stable, as we have described in detail for the related iron(II) complexes,[42] that the chain walking is rapid even at room temperature, and that even alkyl complexes that might give more stable 3-hexenes through β-hydride elimination do not prefer to do so.[59]

These observations most strongly implicate the alkyl mechanism for isomerization, rather than the allyl mechanism. Several additional pieces of evidence supporting this idea will be presented below.

Mechanistic Studies: Alkene Profile. Monitoring the substrate and product concentrations during the reaction was most accurately accomplished using gas chromatography. The reaction profiles for isomerization of 1-hexene under two near-optimal conditions are shown in Figure 6. In both experiments, 1-hexene was consumed quickly in the first 10 h, and then, its concentration remained unchanged; the concentration of *E*-2-hexene increased slowly throughout the reaction time. The concentration of *Z*-2-hexene reached its apex at around 10 h, and then decreased. This degradation of selectivity was more rapid using higher catalyst loading, suggesting that there could be bimolecular decomposition of the selective catalyst over the course of the reaction.

These data suggest a model in which all three of these alkenes are in reversible equilibrium with a common steady-state intermediate (see Supporting Information). However, kinetic fits were underdetermined, and did not yield reliable rate constants. Thus, we were able to use the kinetic data only qualitatively.

Despite the difficulties with quantitative modeling, several lessons may be learned from the product profile. First, the isomerization reaction is reversible, because at very long times the ratio of isomers trends toward the thermodynamic ratio.[48] However, the ratio never reaches the thermodynamic limit, suggesting that the catalyst degrades slowly over time. Second, there are two concurrent processes: rapid isomerization of 1-hexene to *Z*-2-hexene, and a slower isomerization between *Z*-2-hexene and *E*-2-hexene that degrades the initially high *Z*-selectivity. This suggests that later in the reaction when the concentration of 1-hexene is lower, *E*/*Z* isomerization dominates over double bond shifting and thus lowers the selectivity. In order to test this idea, *E*-2-hexene and *Z*-2-hexene were mixed with catalyst **1** separately under standard conditions. Each isomerized toward the thermodynamic ratio very slowly, but *Z*-2-hexene reacted more rapidly than *E*-2-
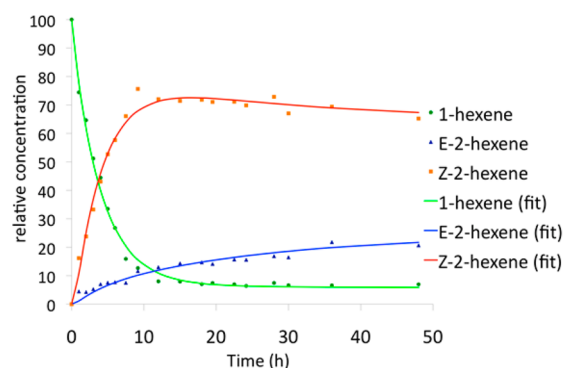
1.0 M 1-hexene, 0.5 mol% catalyst, 80 °C
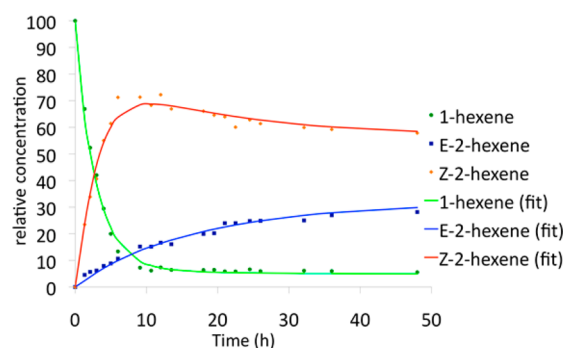
1.0 M 1-hexene, 1.0 mol% catalyst, 80 °C

Figure 6. Concentration profiles of 1-hexene isomerization by **1**. The lines do not represent reliable kinetic models, but help to guide the eye.

hexene. This rate sequence suggests that the *Z* isomer is more easily incorporated into the catalytic cycle. The principle of microscopic reversibility suggests that the *Z*-isomer would also be released more easily by a catalytic intermediate, which agrees with the *Z* selectivity of the catalyst (more detailed reasons for the selectivity will be discussed in detail below).

We hypothesized that the undesired *E*/*Z* isomerization could be slowed by adding an alkene that binds more weakly than 1-hexene but more strongly than *Z*-2-hexene, thus preventing binding and isomerization of *Z*-2-hexene. Table 8 shows that

Table 8. 1-Hexene Isomerization Reaction with Additives

condition	time (h)	yield[a]	*E*:*Z*[a]
0.5 mol % cat., 80 °C, 1.0 M 1-hexene	24	88%	1:4.0
	48	93%	1:1.8
0.5 mol % cat., 5.0 mol % 3,3-dimethyl-1-butene, 80 °C, 1.0 M 1-hexene	24	86%	1:4.6
	48	89%	1:2.4

[a]Yield of products and *E*:*Z* ratios determined by GC analysis.

added 3,3-dimethyl-1-butene to 1-hexene reaction does slow the *E*/*Z* isomerization and maintains *Z*-selectivity for a longer time. Addition of 3,3-dimethyl-1-butene did not significantly improve the performance of aromatic substrates.

Mechanistic Studies: Isotope Labeling. The isomerization of aromatic substrates produced some products in which the C=C double migrates more than one bond. In order to provide a clearer picture of this "chain walking",[29,60−62] we studied the isomerization of (1-^{13}C)-1-hexene, shown in Scheme 4. We monitored the reaction using ^{1}H NMR

spectroscopy after 0−2 h and after 24 h, and the results are shown in Table 9. At the early time points, the ^{13}C label was proximal to the olefin, while after 24 h heating, the ^{13}C label was evenly distributed between the proximal and distal positions. ^{1}H NMR analysis also showed that (6-^{13}C) and (1-^{13}C)-2-hexene have nearly the same E/Z ratio at 24 h.

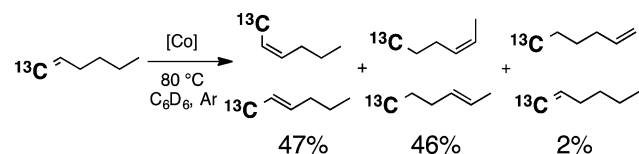**Scheme 4. Isomerization of (1-^{13}C)-1-Hexene with Catalyst 1**

Table 9. Concentrations of Different Species after Placing (1-^{13}C)-1-Hexene under Standard Isomerization Conditions with Catalyst 1^a

	1.0 h	2.0 h	24 h
(1-^{13}C)-1-hexene	64%	44%	1%
(6-^{13}C)-1-hexene^b	9%	11%	1%
(1-^{13}C)-2-hexene	15%	29%	47%
(6-^{13}C)-2-hexene^b	5%	11%	46%

^{a}5 mol % catalyst, 80 °C; yields determined by NMR analysis. ^{b}Due to limitations of the analysis used, up to 5% of unlabeled 1-hexene or 2-hexene derived from exchange with the hexyl group on the catalyst may be included in these values.

Observation of ^{13}C label on both ends of olefins at 0.5 h, before extensive product formation, indicates that chain walking is faster than release of the isomerized product. However, the preference for C1-labeled 2-hexene at early times shows that the rates of chain walking and dissociation of alkene are similar. Further, it shows that product formation is tied to the kinetics of product release, since the E/Z ratio is the same for both isotopologues after 24 h of heating. It is particularly interesting that end-to-end chain walking occurs with 2-hexenes as major products over more stable free 3-hexenes in the product mixture: thus, elimination of 3-hexenes must be kinetically limited by a high barrier.

Mechanistic Studies: Products from Reactions with Protected Alcohols. We serendipitously learned more about the "chain walking" through attempted isomerization of two substrates with protected alcohols (Chart 1). Under standard

Chart 1. Terminal Alkenes Containing Protected Alcohols
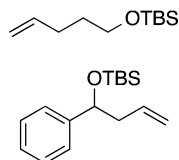
isomerization conditions with catalyst **1**, the paramagnetic products of both reactions were the same, as judged by ^{1}H NMR spectroscopy. This suggested that the cobalt products were siloxide complexes. The siloxide complex was synthesized independently from L^{tBu}CoCl and KOTBS (Scheme 5), and its ^{1}H NMR spectrum matched the paramagnetic peaks at the end of attempted isomerization reactions with TBS-protected alcohols.

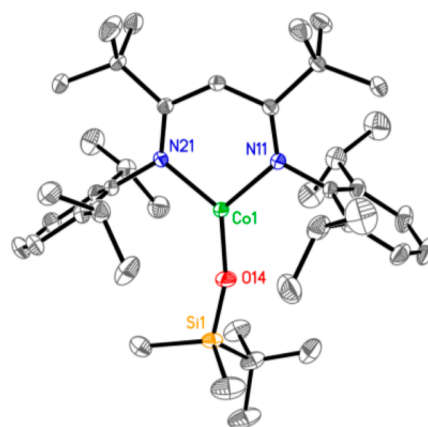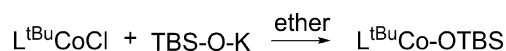**Scheme 5. Independent Synthesis of Cobalt Siloxide Complex**

Figure 7. ORTEP drawing of the molecular structure of L^{tBu}CoOTBS. Thermal ellipsoids at the 50% probability level. Hydrogen atoms omitted for clarity. Important bond distances (Å) and angles (deg): Co−N 1.9277(9), 1.9285(9), Co−O 1.798(4); N−Co−N 97.74(4), Co−O−Si 162.6(3).

The X-ray crystal structure of L^{tBu}CoOTBS is shown in Figure 7. The Co−N bond distances in L^{tBu}CoOTBS are similar to the Co−N bond distances in other L^{tBu}Co^{II} complexes.[43] The Co−O bond distance of 1.799(1) Å is similar to the Fe−O distances in L^{Me}FeO^{t}Bu (1.78(1) Å)[63] and L^{tBu}FeO^{t}Bu (1.786(3) Å).[64] The N−Co−N angle is 97.74(4)°, and the N−Co−O angles are 133.2(1)° and 129.0(1)°; the sum of 359.9° indicates that the cobalt center is planar. Like other cobalt(II) complexes mentioned above, the ^{1}H NMR spectrum shows paramagnetically shifted resonances consistent with C_{2v} symmetry; this indicates that the TBS group rotates around the C_2 axis rapidly on the NMR time scale.

We attribute the formation of L^{tBu}CoOTBS to chain walking followed by β-alkoxide elimination; note that chain walking was also implied by the ^{13}C labeling experiments above. We also considered the possibility that the cobalt-OTBS species could result from direct reaction with the C−O bond by a cobalt hydride through a four-membered transition state, but reactions with *tert*-butyldimethyl(octyloxy)silane and *tert*-butyldimethyl-(3-phenylpropoxy)silane, which lack an alkene, did not form a siloxide product. Thus, the elimination could be blocked by preventing cobalt center from approaching OTBS.

The above concept suggests that siloxy groups might be tolerated if chain walking were slowed. This was achieved through adding steric hindrance. For example, a ketal (Table 4, entry 12) is tolerated, perhaps since its C−O bonds are on a hindered quaternary center. Tolerance of OTBS groups can be achieved by simply introducing a methyl group between the alkene and the siloxy group, as shown in Table 4, entry 11. Each of these observations is fully consistent with the proposed β-alkoxide elimination mechanism.

■ **DISCUSSION**

Isomerization Mechanism. We find that the isomerization of terminal alkenes to 2-alkene isomers can be catalyzed by both the cobalt(II) complex L^{tBu}Co(*n*-hexyl) (**1**) and the cobalt(I) complex L^{tBu}Co (**2**). Since these high-spin catalysts

Scheme 6. Proposed Mechanism of 1-Hexene Isomerization
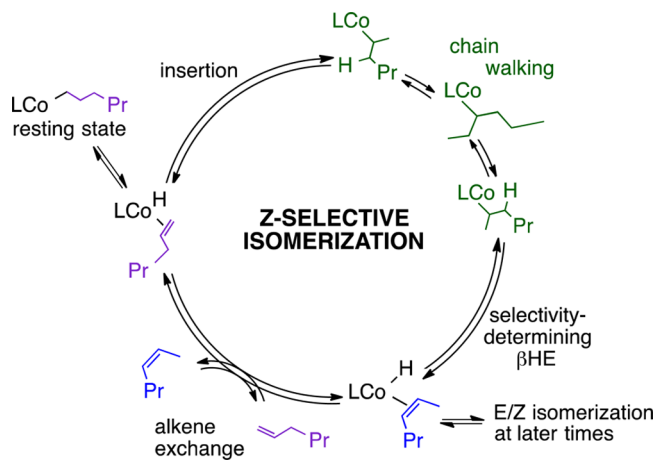
have electrons in M−L σ-antibonding orbitals, one might be concerned that they could suffer metal−ligand dissociation, giving a catalyst that is actually a soluble or insoluble metal cluster or nanoparticle. In the case of catalyst **2**, this fear appears to have been realized, because addition of Hg eliminates activity. In contrast, with catalyst **1**, addition of Hg or PPh₃ has no significant effect on reactivity and selectivity, which supports the idea that *isomerization of alkenes by catalyst 1 is homogeneous.*[65,66] For this reason, only catalysis by **1** was studied in detail.

As mentioned in the Introduction, there are two predominant mechanisms for alkene isomerization in the literature, which are distinguished by the active intermediates with an M−C bond. In this system, observation of an alkylcobalt(II) species as the resting form, the lack of a significant induction period for catalysis by a cobalt-alkyl complex, the ability of an ethylcobalt-(II) complex to convert to a hexylcobalt(II) complex with 1-hexene, and the rapid isomerization of a 3-hexyl complex to a 1-hexyl complex serve as strong evidence in support of the alkyl mechanism (Scheme 1a). Isomerization between double bond positions, and between alkyl isomers, is explained through chain walking through reversible β-hydride elimination from the alkyl complex.

The idea that the alkyl mechanism is facile is also supported by our recently reported DFT computations on truncated diketiminate-bound cobalt(II) alkyl complexes, which indicated a barrier of only 13 kcal/mol for β-hydride elimination and 1.2 kcal/mol for alkene insertion into a transient cobalt-hydride species.[67] Though these barriers are expected to be higher with the bulky ligand described here, the computations support the presence of a feasible pathway for the key β-hydride elimination and alkene insertion steps.

We propose the mechanism shown in Scheme 6 for isomerization of 1-hexene to Z-2-hexene. The off-cycle 1-hexyl complex is the spectroscopically observed resting state. Note that chain walking occurs before alkene exchange, which is needed to explain the ¹³C labeling results. The high Z-selectivity at early times shows that the selectivity-determining β-hydride elimination preferentially gives the Z-alkene hydride complex. At later times, 1-hexenes are depleted, slowing the alkene exchange, and competitive pathways (E−Z isomerization) can degrade the selectivity. Added 3,3-dimethylbutene can displace the 2-alkenes (blue) but not the productive 1-alkene (purple), which reduces the concentration of the

potentially problematic 2-alkene complex shown at the bottom of the cycle.

The cobalt-catalyzed transformation of terminal alkenes to 2-alkenes, without forming observable stable 3-alkenes, initially suggested that chain walking from the terminal alkene might be limited to one step followed by elimination, as seen in other metal-hydride catalyzed alkene isomerizations.[68] However, this hypothesis was dispelled by the observation that ¹³C labeling on one end of the initial alkene led to products with ¹³C label on both ends, but similar E/Z ratios. This result shows that both the selectivity and stereoselectivity are determined by the elimination step.

Z-Selectivity in Alkene Isomerization by LᵗᴮᵘCo(n-hexyl). The catalytic isomerization of terminal alkenes by **1** does not reach equilibrium. The order in thermodynamic stability of hexene isomers is the following: E-3-hexene (ΔH°_f = −86.1 kJ/mol), E-2-hexene (ΔH°_f = −85.5 kJ/mol), Z-2-hexene (ΔH°_f = −83.9 kJ/mol), Z-3-hexene (ΔH°_f = −78.9 kJ/mol), 1-hexene (ΔH°_f = −74.2 kJ/mol).[48] These heats of formation are close enough that one would expect to see a mixture of isomers at equilibrium, and predominantly E-stereochemistry. The ability of LᵗᴮᵘCo(n-hexyl) to selectively produce the 2-Z-hexene is thus kinetically controlled.

In a few examples in the literature, there was a preference for the less thermodynamically stable Z isomer. In most cases, this was brought about by directing groups.[33,34,68,69] In a few cases, there was slight Z-selectivity at the beginning of the reaction,[32,69] but it degraded rapidly. Most previous cases of Z-selectivity were interpreted as arising from the allyl mechanism, with the exception of ReBrH(NO)(dppfc), where the initially formed 1:1 mixture of E- and Z-isomers eventually isomerized to predominantly E-2-hexene.[68] In this context, it is interesting that LᵗᴮᵘCo(n-hexyl) catalyzes isomerizations with Z-selectivities of up to 12:1 without metal-binding functional groups. The Z-selectivity of the LᵗᴮᵘCo(n-hexyl)-catalyzed isomerization degrades at longer times, because the thermodynamic preference for E-isomers inevitably asserts itself and because the catalyst degrades to a product that is active for isomerization but not selective. Thus, choosing the appropriate reaction time is important: longer times give greater conversion, but in some cases this comes at the expense of lower stereoselectivity and/or regioselectivity in the products.

Steric Model For Selectivity. In the isomerization mechanism in Scheme 6, the proposed selectivity-determining step is β-hydride elimination. Although LᵗᴮᵘCo(hexyl) has an S = ³/₂ ground state, previous computational studies[67] have shown that the lowest barrier for β-hydride elimination is on the doublet (S = ¹/₂) potential energy surface that arises from rapid spin crossover. Interestingly, these DFT studies found that the transition state has a *square-planar geometry*, treating the β-hydride as one of the ligands.

This transition-state geometry is the key to rationalizing the Z-selectivity of the catalyst. Due to the choice between two β-hydrogens, there are two distinct rotamers of the transition state for β-hydride elimination from LᵗᴮᵘCo(2-hexyl) (Figure 8). These different rotamers determine whether the E- or Z-alkene will be formed in the β-hydride elimination. Hindrance is lessened in the Z-rotamer because the incipient bound alkene can "roll" in order to place both alkene substituents between the bulky isopropyl groups of the supporting ligand (Figure 8, upper left). On the other hand, the E-isomer cannot reach a conformation that achieves the key pseudo-square-planar
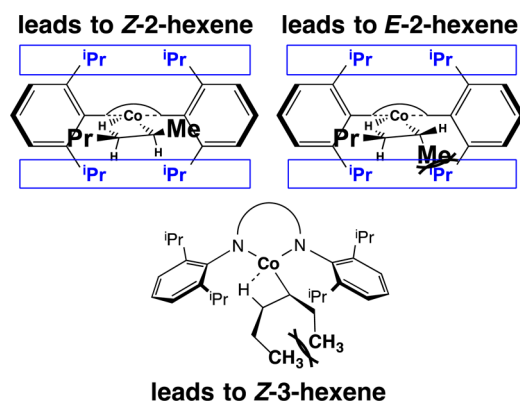
Figure 8. Steric model explaining the regioselectivity and stereo-selectivity of alkene isomerization by the bulky cobalt catalyst. In the transition state leading to *E*-2-hexene (upper right), one of the alkyl substituents suffers a steric clash with the isopropyl groups. The transition state leading to 3-hexenes (bottom) is constrained by the aryl groups to give an unfavorable *syn*-pentane-like conformation.

geometry at Co without suffering severe steric interactions between the methyl substituent and the diketiminate ligand (Figure 8, upper right). This also explains why the diketiminate supporting ligand is especially effective: this ligand electronically enforces a square-planar transition state, while sterically constraining substrate substituents to a narrow cleft between the isopropyl groups. The unusual selectivity for 2-alkenes over 3-alkenes is also rationalized by the bulky steric environment of the diketiminate-cobalt catalyst. The key transition state leading to 3-hexene (Figure 8, bottom) has two ethyl groups that are conformationally constrained by the bulky ligands, in a way that forces the ethyl groups together in a manner reminiscent of the well-known *syn*-pentane interaction.[70] In accordance with a steric explanation for the selectivity, preliminary experiments with less-bulky diketiminate ligands show neither regioselectivity nor stereoselectivity.

The mechanism proposed in Scheme 6 requires that the unfavorable transition states in Figure 8 are not so high as to be completely inaccessible, because chain walking requires β-hydride elimination through an olefin hydride complex of the 3-hexene. However, the alkene exchange step is likely to have similar steric constraints. Future computational studies will test this steric model quantitatively. However, the qualitative model in Figure 8 is an initial guide for further catalyst development.

Scope of Catalytic Z-Selective Isomerization. Though linear substrates might be expected to give low selectivity due to the lack of functional groups, the regioselectivity of the cobalt-catalyzed reaction is very good for isomerization of 1-hexene to *Z*-2-hexene. In this case, trace 3-hexenes are observed only after the reaction is continued for 24 h or longer. Limiting the reaction time to 12 h gives an *E/Z* selectivity of 1:4 to 1:5, and selectivity is best when the catalyst loading is kept low (presumably avoiding bimolecular catalyst decomposition). With longer linear alkenes, the *E/Z* selectivity is also very good, though increasing the chain length lowers the regioselectivity. This can be controlled to some extent by shortening the reaction time, though the conversion is lower.

The cobalt-catalyzed reaction provides a route to functionalized 2-alkenes. For example, a homoallylsilane was converted specifically into the *Z*-crotylsilane with more than 90% selectivity. Crotylsilanes are synthetically useful for allylations of carbonyls,[71] acetals,[72] and enones.[73,74] A cobalt catalyst for

selective isomerization of homoallylsilanes and allylsilanes to *E*-crotylsilanes and *E*-vinylsilanes is known.[75]

The isomerization does not tolerate weakly acidic functional groups such as alcohols and ketones, though protected versions of these substrates (silyl esters and ketals) can be transformed with excellent *Z*-selectivity. Though linear siloxy substituents cause catalyst degradation through chain walking and β-siloxy elimination, OTBS elimination is not observed when there is one or more methyl groups in the chain between the alkene and the protected alcohol. Because functionalized substrates are much more common than linear substrates, it is likely that most TBS-protected alcohols can be used as substrates.

Initial experiments with aromatic alkenes gave low conversions, probably because of a bimolecular reaction.[76] Lowering the catalyst concentration restored the *Z*-selectivity to a level comparable to that of the aliphatic substrates, except for styrenes. In the long run, we anticipate that modification of the catalyst will ameliorate some of the incompatibilities, and selectivity can be improved by using the steric model of selectivity in Figure 8.

■ CONCLUSIONS

The β-diketiminate cobalt(II) complex **1** catalyzes the isomerization of terminal alkenes selectively to 2-alkenes with *Z*-stereochemistry. Mechanistic studies on 1-hexene isomerization show that the cobalt(II) catalyst walks rapidly along the hexyl group, yet it selectively eliminates the *Z*-isomer of 2-hexene rather than other isomers of lower energy. The selectivity can be explained by a steric model, which should inform the future design of new catalysts with improved *Z*-selectivity.

The selectivity for the transformation of 1-hexene is particularly notable considering that there are no directing groups on the substrate. Other terminal alkenes can be used as well, including synthetically useful silanes, ketals, and protected alcohols. Deleterious reactions with certain polyenes and silyl-protected alcohols can be controlled by modifying the catalyst concentration and substrate structure. Most importantly, the models for the mechanism and selectivity lay the groundwork for rational design of additional catalysts for selective alkene isomerization with greater robustness and reaction scope.

■ EXPERIMENTAL SECTION

General Considerations. All reagents were purchased from commercial sources and were dried over activated alumina and then stored over 3 Å molecular sieves. Glassware was dried at 150 °C overnight, and Celite was dried overnight at 200 °C under vacuum. Pentane, hexane, benzene, diethyl ether, and toluene were purified by passage through activated alumina and Q5 columns from Glass Contour Co. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and dried over activated alumina.

NMR spectra were recorded on Bruker Avance 400 or 500 NMR spectrometers, at roughly 295 K. All resonances in the ^{1}H NMR spectra are referenced to residual protiated benzene (δ 7.16 ppm) or chloroform (δ 7.26 ppm). Resonances were singlets unless otherwise noted. The NMR probe temperature was calibrated using either ethylene glycol or methanol.[77,78] IR data were recorded on a Shimadzu FTIR spectrophotometer (FTIR-8400S) using a KBr pellet. UV–vis spectra were recorded on a Cary 50 spectrophotometer using airtight cuvettes with a 1 mm optical path length. Solution magnetic susceptibilities were determined by the Evans method.[79,80] Elemental analyses were obtained from the CENTC Elemental Analysis Facility at the University of Rochester. Further chromatographic details are given in the Supporting Information.

L^{tBu}Co(*n*-hexyl). Under argon atmosphere, hexylmagnesium bromide (0.84 mL, 2.0 M in THF, 1.7 mmol) was added dropwise to a

solution of L^{tBu}CoCl[43] (989 mg, 1.66 mmol) in dry toluene (80 mL). The suspension was stirred at room temperature for 1 h, and the color changed to dark red-brown. Volatile materials were removed under vacuum. The solid was extracted with pentane (80 mL), filtered through Celite, and concentrated to 4.0 mL. Hexamethyldisiloxane (4.0 mL) was added, and the solution was cooled to −40 °C to give red-brown crystals (407 mg, 74%). ^{1}H NMR (C$_6$D$_6$, 25 °C) δ −120.0 (12H, iPr methyl), −52.9 (1H, α-H), −50.9 (4H), −28.3 (2H), 3.8 (12H, iPr methyl), 4.2 (2H), 9.8 (2H), 11.3 (2H), 18.0 (2H), 27.0 (18H, tBu), 73.3 (4H), 242.0 (2H). The resonances that integrate for 4H can be assigned as ^{i}Pr-methine or aryl m-H. The resonances that integrate for 2H can be assigned as aryl p-H or methylene in n-hexyl group. μ_{eff} (Evans, C$_6$D$_6$, 299.2 K) = 4.9(1) μ_B. UV−vis (pentane): 278 nm (ε = 14.6 mM^{-1} cm^{-1}), 332 nm (ε = 12.9 mM^{-1} cm^{-1}), 468 nm (ε = 1.2 mM^{-1} cm^{-1}), 736 nm (ε = 0.1 mM^{-1} cm^{-1}). Anal. Calcd for C$_{41}$H$_{66}$N$_2$Co: C, 76.24; H, 10.32; N, 4.34. Found: C, 76.07; H, 10.52; N, 4.12. IR (KBr, cm^{-1}): 3055 (w), 2958 (vs), 2924 (s), 2870 (m), 1508 (m), 1431 (m), 1383 (s), 1364 (vs), 1317 (m), 1251 (w), 1221 (w), 1155 (w), 1097 (m), 1055 (m), 1030 (w), 933 (w), 845 (w), 802 (w), 777 (m), 756 (w), 711 (w).

L^{tBu}Co(η^2-allylbenzene). Under argon atmosphere, allylbenzene (225 μL, 0.46 mmol) was added to a solution of L^{tBu}Co[47] (261 mg, 0.46 mmol) in dry diethyl ether (5.0 mL). The mixture was stirred at room temperature for 0.5 h, and the color changed to dark red-brown. Volatile materials were removed under vacuum. The solid was extracted with pentane (10 mL), filtered through Celite, and concentrated to 2.0 mL. Hexamethyldisiloxane (2.0 mL) was added, and the solution was cooled to −40 °C to give red-brown crystals (256 mg, 81%). ^{1}H NMR (500 MHz, C$_6$D$_6$) δ −101.5 (2H), −87.8 (6H, iPr methyl), −47.2 (6H, iPr methyl), −27.4 (2H), −21.4 (2H), −17.4 (6H, iPr methyl), −11.8 (1H), −4.1 (6H, iPr methyl), −2.2 (2H), 11.9 (2H), 18.5 (1H), 22.0 (18H, backbone tBu), 44.2 (2H), 57.7 (1H), 227.7 (1H). The resonances that integrate for 2H can be assigned as iPr methine, aryl m-H, aryl m-H (allyl benzene), aryl o-H (allyl benzene), or benzyl-H (allyl benzene). The resonances that integrate for 1H can be assigned as aryl p-H or α-H. The alkene protons are presumably broadened into the baseline by the nearby paramagnetic metal. μ_{eff} (Evans, C$_6$D$_6$, 295.8 K) = 3.8(1) μ_B. UV−vis (pentane): 550 nm (ε = 0.47 mM^{-1} cm^{-1}). Anal. Calcd for C$_{41}$H$_{66}$N$_2$Co: C, 77.68; H, 9.26; N, 4.21. Found: C, 77.87; H, 9.67; N, 4.04. IR (KBr, cm^{-1}): 3057 (w), 3024 (w), 2959 (vs), 2927 (s), 2868 (m), 2385 (w), 1913 (w), 1855 (w), 1797 (w), 1541 (m), 1506 (s), 1463 (w), 1435 (m), 1388 (vs), 1359 (s), 1317 (s), 1286 (w), 1252 (w), 1217 (m), 1188 (m), 1155 (w), 1132 (w), 1095 (m), 1055 (w), 1028 (w), 934 (w), 885 (w), 806 (w), 773 (m), 740 (m), 694 (m), 574 (w), 534 (m, br).

L^{tBu}Co(OTBS). Under an argon atmosphere, a solution of tert-butyl(dimethyl)silanol (21 mg, 0.16 mmol) in ether (2.0 mL) was added dropwise to a suspension of KH (6.4 mg, 0.16 mmol) in ether (2.0 mL). The reaction mixture was stirred at room temperature for 1 h and filtered through Celite into a solution of L^{tBu}CoCl[43] (92 mg, 0.15 mmol) in dry ether (2.0 mL). The suspension was stirred at room temperature for 1 h, and the color changed to green. Volatile materials were removed under vacuum. The solid was extracted with pentane (10 mL) and filtered through Celite to give a green solution, which was concentrated to 2.0 mL. Hexamethyldisiloxane (2.0 mL) was added, and the solution was cooled to −40 °C to give green crystals (47.9 mg, 45%). ^{1}H NMR (500 MHz, C$_6$D$_6$) δ −89.0 (1H, α-H), −71.5 (12H, iPr methyl), −34.9 (4H) −31.8 (2H, aryl p-H), −0.6 (12H, iPr methyl), 12.8 (9H, OTBS, tBu), 17.0 (6H, OTBS, methyl), 21.1 (18H, backbone tBu), 56.0 (4H). The resonances that integrate for 4H can be assigned as iPr-methine or aryl m-H. μ_{eff} (Evans, C$_6$D$_6$, 295.8 K) = 4.8(1) μ_B. UV−vis (pentane): 585 nm (sh, ε = 0.16 mM^{-1} cm^{-1}), 605 nm (ε = 0.16 mM^{-1} cm^{-1}), 645 nm (ε = 0.16 mM^{-1} cm^{-1}). Anal. Calcd for C$_{41}$H$_{67}$N$_2$OSiCo: C, 71.26; H, 9.77; N, 4.05. Found: C, 71.48; H, 10.17; N, 4.00. IR (KBr, cm^{-1}): 3061 (m), 3014 (m), 2960 (vs), 2928 (s), 2872 (s), 2385 (w), 1923 (w), 1860 (w), 1800 (w), 1535 (m), 1506 (s), 1464 (m), 1435 (m), 1375 (s), 1360 (vs), 1317 (s), 1246 (m), 1217 (w), 1196 (m), 1136 (w), 1098 (m), 1057 (w), 982 (vs), 827 (m), 806 (w), 766 (m), 669 (m), 530 (m, br).

General Procedure for Alkene Isomerization. Alkenes were degassed, and dried using 4 Å molecular sieves; multiple treatments were generally necessary to make the alkenes dry enough to prevent catalyst degradation. To a resealable NMR tube was added 1-alkene (0.50 mmol), mesitylene (69.5 μL, 0.50 mmol), L^{tBu}Co(n-hexyl) (0.025 mmol, 5.0% catalyst loading), and C$_6$D$_6$ (0.50 mL). The reaction mixture was heated at 80 °C and monitored by ^{1}H NMR spectroscopy. After 24 h, the reaction mixture was opened to air and filtered through a short silica pad (1.5 cm) in a disposable pipet to remove Co-containing species. The filtrate was analyzed by ^{1}H NMR spectroscopy and GC/MS. Details are in the Supporting Information.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Additional kinetic, spectroscopic, and crystallographic data (CIF), and details on the synthesis of organic compounds and catalytic reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors
weix@chem.rochester.edu
patrick.holland@yale.edu

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Siau, W.-Y.; Zhang, Y.; Zhao, Y. *Top. Curr. Chem.* **2012**, *327*, 33.
(2) Vedejs, E.; Peterson, M. J. *Top. Stereochem.* **1994**, *21*, 1.
(3) Bergelson, L. D.; Shemyakin, M. M. *Tetrahedron* **1963**, *19*, 149.
(4) Still, W. C.; Gennari, C. *Tetrahedron Lett.* **1983**, *24*, 4405.
(5) Hegedus, L. S.; Söderberg, B. C. G. *Transition Metals in the Synthesis of Complex Organic Molecules*, 3rd ed.; University Science Books: Sausalito, CA, 2009.
(6) Lindlar, H.; Dubuis, R. *Org. Synth.* **1966**, *46*, 89.
(7) Katz, T. J.; McGinnis, J.; Altus, C. *J. Am. Chem. Soc.* **1976**, *98*, 606.
(8) Ibrahem, I.; Yu, M.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 3844.
(9) Endo, K.; Grubbs, R. H. *J. Am. Chem. Soc.* **2011**, *133*, 8525.
(10) Herrmann, W. A.; Prinz, M. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Eds.; Wiley: New York, 2002; Vol. 3, p 111.
(11) van Leeuwen, P. W. N. M. *Homogeneous Catalysis*; Kluwer: Dordrecht, 2004.
(12) Hubert, A. J.; Reimlinger, H. *Synthesis* **1969**, 97.
(13) Hubert, A. J.; Reimlinger, H. *Synthesis* **1970**, 405.
(14) Baudry, D.; Ephritikhine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1978**, 694.
(15) Biswas, S.; Huang, Z.; Choliy, Y.; Wang, D. Y.; Brookhart, M.; Krogh-Jespersen, K.; Goldman, A. S. *J. Am. Chem. Soc.* **2012**, *134*, 13276.
(16) Canovese, L.; Visentin, F. *Inorg. Chim. Acta* **2010**, *363*, 2375.
(17) Scarso, A.; Colladon, M.; Sgarbossa, P.; Santo, C.; Michelin, R. A.; Strukul, G. *Organometallics* **2010**, *29*, 1487.
(18) Donohoe, T. J.; O'Riordan, T. J. C.; Rosa, C. P. *Angew. Chem., Int. Ed.* **2009**, *48*, 1014.
(19) Sivaramakrishna, A.; Mushonga, P.; Rogers, I. L.; Zheng, F.; Haines, R. J.; Nordlander, E.; Moss, J. R. *Polyhedron* **2008**, *27*, 1911.

(20) Price, C. C.; Snyder, W. H. *J. Am. Chem. Soc.* **1961**, *83*, 1773.

(21) Fu, G. C. In *Modern Rhodium-Catalyzed Organic Reactions*; Evans, P. A., Ed.; Wiley-VCH: Weinheim, 2005; p 79.

(22) Wille, A.; Tomm, S.; Frauenrath, H. *Synthesis* **1998**, 305.

(23) Kuba, S.; Gates, B. C.; Grasselli, R. K.; Knozinger, H. *Chem. Commun.* **2001**, 321.

(24) Roos, L.; Orchin, M. *J. Am. Chem. Soc.* **1965**, *87*, 5502.

(25) Coperet, C. *Beilstein J. Org. Chem.* **2011**, *7*, 13.

(26) Krompiec, S.; Kuznik, N.; Penczek, R.; Rzepa, J.; Mrowiec-Bialon, J. *J. Mol. Catal. A: Chem.* **2004**, *219*, 29.

(27) Larsen, C. R.; Grotjahn, D. B. *Top. Catal.* **2010**, *53*, 1015.

(28) Gauthier, D.; Lindhardt, A. T.; Olsen, E. P. K.; Overgaard, J.; Skrydstrup, T. *J. Am. Chem. Soc.* **2010**, *132*, 7998.

(29) Grotjahn, D. B.; Larsen, C. R.; Gustafson, J. L.; Nair, R.; Sharma, A. *J. Am. Chem. Soc.* **2007**, *129*, 9592.

(30) Larsen, C. R.; Grotjahn, D. B. *J. Am. Chem. Soc.* **2012**, *134*, 10357.

(31) Grotjahn, D. B. *Pure Appl. Chem.* **2010**, *82*, 635.

(32) Tuner, M.; Jouanne, J. v.; Brauer, H. D.; Kelm, H. *J. Mol. Catal.* **1979**, *5*, 433.

(33) Sato, T.; Komine, N.; Hirano, M.; Komiya, S. *Chem. Lett.* **1999**, 441.

(34) Pünner, F.; Schmidt, A.; Hilt, G. *Angew. Chem., Int. Ed.* **2012**, *51*, 1270.

(35) Ohmura, T.; Yamamoto, Y.; Miyaura, N. *Chem. Commun.* **1998**, 1337.

(36) Tani, K.; Yamagata, T.; Akutagawa, S.; Kumobayashi, H.; Taketomi, T.; Takaya, H.; Miyashita, A.; Noyori, R.; Otsuka, S. *J. Am. Chem. Soc.* **1984**, *106*, 5208.

(37) Krompiec, S.; Pigulla, M.; Krompiec, M.; Marciniec, B.; Chadyniak, D. *J. Mol. Catal. A: Chem.* **2005**, *237*, 17.

(38) Crabtree, H. R. In *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Wiley-Interscience: New York, 2005, p 239.

(39) Poli, R. *Chem. Rev.* **1996**, *96*, 2135.

(40) Poli, R. *J. Organomet. Chem.* **2004**, *689*, 4291.

(41) Vela, J.; Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *Chem. Commun.* **2002**, 2886.

(42) Vela, J.; Vaddadi, S.; Cundari, T. R.; Smith, J. M.; Gregory, E. A.; Lachicotte, R. J.; Flaschenriem, C. J.; Holland, P. L. *Organometallics* **2004**, *23*, 5226.

(43) Holland, P. L.; Cundari, T. R.; Perez, L. L.; Eckert, N. A.; Lachicotte, R. J. *J. Am. Chem. Soc.* **2002**, *124*, 14416.

(44) Ding, K.; Brennessel, W. W.; Holland, P. L. *J. Am. Chem. Soc.* **2009**, *131*, 10804.

(45) Ding, K.; Dugan, T. R.; Brennessel, W. W.; Bill, E.; Holland, P. L. *Organometallics* **2009**, *28*, 6650.

(46) Ding, K.; Dugan, T. R.; Holland, P. L.; Adhikari, D.; Mindiola, D. J. *Inorg. Synth* **2010**, *35*, 43.

(47) Dugan, T. R.; Sun, X.; Rybak-Akimova, E. V.; Olatunji-Ojo, O.; Cundari, T. R.; Holland, P. L. *J. Am. Chem. Soc.* **2011**, *133*, 12418.

(48) *Handbook of Chemistry and Physics*, 73rd ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1993.

(49) Crabtree, R. H. *Chem. Rev.* **2012**, *112*, 1536.

(50) Yu, Y.; Smith, J. M.; Flaschenriem, C. J.; Holland, P. L. *Inorg. Chem.* **2006**, *45*, 5742.

(51) Cochran, J. C.; Hagen, K. r.; Paulen, G.; Shen, Q.; Tom, S.; Traetteberg, M.; Wells, C. *J. Mol. Struct.* **1997**, *413*, 313.

(52) Bai, G.; Wei, P.; Das, A. K.; Stephan, D. W. *Dalton Trans.* **2006**, 1141.

(53) Trupia, S.; Bitterwolf, T. E.; Geiger, W. E. *Organometallics* **2012**, *31*, 6063.

(54) Cabelli, D. E.; Shafiq, F.; Creutz, C.; Bullock, R. M. *Organometallics* **2001**, *20*, 3729.

(55) Berning, D. E.; Noll, B. C.; DuBois, D. L. *J. Am. Chem. Soc.* **1999**, *121*, 11432.

(56) Bullock, R. M. *Comments Inorg. Chem.* **1991**, *12*, 1.

(57) Estes, D. P.; Norton, J. R.; Jockusch, S.; Sattler, W. *J. Am. Chem. Soc.* **2012**, *134*, 15512.

(58) Barratt, D. S.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1559.

(59) Free 3-hexenes could not be generated quickly and then completely consumed by the catalyst, because their quantitative isomerization to other isomers is thermodynamically unfavorable.

(60) Chen, G.; Ma, X. S.; Guan, Z. *J. Am. Chem. Soc.* **2003**, *125*, 6697.

(61) Kochi, T.; Hamasaki, T.; Aoyama, Y.; Kawasaki, J.; Kakiuchi, F. *J. Am. Chem. Soc.* **2012**, *134*, 16544.

(62) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**, *283*, 2059.

(63) Eckert, N. A.; Smith, J. M.; Lachicotte, R. J.; Holland, P. L. *Inorg. Chem.* **2004**, *43*, 3306.

(64) Gibson, V. C.; Marshall, E. L.; Navarro-Llobet, D.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2002**, 4321.

(65) Widegren, J. A.; Finke, R. G. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317.

(66) Crabtree, R. H. *Chem. Rev.* **2011**, *112*, 1536.

(67) Bellows, S. M.; Cundari, T. R.; Holland, P. L. *Organometallics* **2013**, *32*, 4741−4751.

(68) Dudle, B.; Rajesh, K.; Blacque, O.; Berke, H. *J. Am. Chem. Soc.* **2011**, *133*, 8168.

(69) Pines, H.; Schaap, L. A. *Adv. Catal.* **1960**, *12*, 117.

(70) Hoffmann, R. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 2054.

(71) Denmark, S. E.; Fu, J. *Chem. Rev.* **2003**, *103*, 2763.

(72) Hosomi, A.; Ando, M.; Sakurai, H. *Chem. Lett.* **1986**, *15*, 365.

(73) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063.

(74) Pan, L.-R.; Tokoroyama, T. *Chem. Lett.* **1990**, *19*, 1999.

(75) Kobayashi, T.; Yorimitsu, H.; Oshima, K. *Chem.—Asian J.* **2009**, *4*, 1078.

(76) Tan, E. H. P.; Lloyd-Jones, G. C.; Harvey, J. N.; Lennox, A. J. J.; Mills, B. M. *Angew. Chem., Int. Ed.* **2011**, *50*, 9602.

(77) Ammann, C.; Meier, P.; Merbach, A. E. *J. Magn. Reson.* **1982**, *46*, 319.

(78) Kaplan, M. L.; Bovey, F. A.; Cheng, H. N. *Anal. Chem.* **1975**, *47*, 1703.

(79) Baker, M. V.; Field, L. D.; Hambley, T. W. *Inorg. Chem.* **1988**, *27*, 2872.

(80) Schubert, E. M. *J. Chem. Educ.* **1992**, *69*, 62.