Reversible 1,2-Methyl Migration to an N-Heterocyclic Carbene in a $PC_{NHC}P$ Cobalt(I) Complex Enables Stereoselective (*E* and *Z*) Allyl Ether Isomerization.

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Supporting Information Placeholder

ABSTRACT: With growing efforts pushing towards sustainable catalysis, using earth-abundant metals has become increasingly important. Here we present the first examples of cobalt PC_{NHC}P pincer complexes that demonstrate dual stereoselectivity for allyl ether isomerization. While the cationic cobalt complex $[((PC_{NHC}P)Co)_2 - \mu - N_2][BAr_4F]_2$ (3) affords the Z-isomer of the enol ether predominantly, the corresponding methyl complex [(PC_{NHC}P)CoMe)] (4) mostly gives the *E*-isomer. The dichotomy in selectivity is investigated computationally, revealing important contributions from the steric profile of the substituents on the metal (Me or N_2), including an unprecedented migration of the methyl substituent from cobalt to the Nheterocyclic carbene carbon, which is further explored in this report.

INTRODUCTION

The carbon-carbon double bond, i.e., an alkene, is an important constituent of many organic compounds that are relevant in natural and industrial products.¹ Among the variety of methods available to install it,² the selective transposition of a carbon-carbon double bond has become an attractive choice for the synthesis of these important skeletal fragments.³ Typically, the transposition is catalyzed by a precious metal such as palladium,⁴ ruthenium,⁵ or iridium.⁶ However, in recent years more environmentally friendly alternatives, based on earth-abundant metals such as iron,⁷ cobalt,⁸ and nickel,⁹ have been developed as well.¹⁰ Irrespective of the metal, the isomerization occurs via distinct mechanistic pathways that proceed via a (i) metal-allyl,¹¹ (ii) metal-alkyl,¹² or (iii) radical intermediate,^{9b, 13} which allows for distinct reaction profiles to be developed for the synthesis of these useful and value-added products.14

The type of mechanism, however, can have important consequences for the stereoselectivity of the reaction.^{11a} In an alkyl-type mechanism the stereoselectivity is usually determined during β -hydride elimination from a metal-alkyl species. However, discriminating between the nearly identical β -hydrogens is challenging, resulting in erosion of the stereoselectivity. In contrast, in an allyl-type mechanism, the differences in 1,2– or 1,3–allylic strain may be used to control the stereoselectivity. However, *Z*-alkenes are kinetically and thermodynamically disfavored,¹⁵ resulting in very few reported *Z*-selective alkene isomerization catalysts.^{8d, h, k, m, 9c, 16} (**Figure 1**). Mechanistically, almost all the *Z*-selective alkene isomerization reactions proceed via an alkyl-type mechanism. The origin of the observed selectivity is,





Figure 1. Selected examples of *Z*-selective cobalt catalyzed alkene isomerization, and the herein reported ligand effects for dual selectivity (*E* and *Z*) in allyl ether isomerization.

Scheme 1. Synthesis of cobalt complexes 1-4.



unfortunately, often underexplored. In a rare example, Holland and co-workers determined that steric factors were mainly responsible for the observed Z-selectivity in alkene isomerization with a cobalt(II)alkyl complex.^{8m} Interestingly, when the catalyst was exchanged for a cobalt(I) η^{6} -arene species, not only was a switch to the more uncommon allyl mechanism observed, further mechanistic studies also revealed that a spin-state change of the cobalt metal center was responsible for the observed Z-selectivity.^{8d} Besides these studies, mechanistic information regarding the origin of the observed stereoselectivity is limited in alkene isomerization, hampering the development of Z-selective alkene isomerization catalysts.

Recently, we reported the synthesis of an anionic iron(0) hydride complex supported by a PC_{NHC}P pincer ligand with a N-heterocyclic carbene as a central donor.^{7b} This complex proved to be extremely active for the selective one-bond isomerization of a variety of alkenes. Since our mechanistic studies indicated a spin-accelerated alkyl-type mechanism, we became interested in developing new reaction methodologies that rely on an allyl-type rather than an alkyl-type mechanism to improve Z-stereo-selectivity. Herein, we present the first examples of cobalt PC_{NHC}P pincer complexes (Figure 1) that show orthogonal selectivity (E vs. Z) for allyl ether isomerization, despite having nearly identical ligands and overall structure. The isomerization occurs under moderate conditions and supports a wide variety of functional groups. Experimental and computational studies were used to provide a better mechanistic understanding regarding the origins of the dichotomy between the stereoselectivity of complexes 3(Z) and 4(E). The experimental studies revealed a classical allyl-type mechanism and computational studies showed interesting ligand effects (N_2 vs Me), where an unprecedented migration of the methyl substituent from cobalt to the NHC carbon enables the *E*-selective isomerization with complex 4. By contrast, N₂ dissociation in complex 3 favors a more Z-selective pathway for allyl ether isomerization, which is further discussed in this report.

RESULTS AND DISCUSSION

Synthesis of cobalt $PC_{NHC}P$ pincer complexes

To develop the necessary methodology for *Z*-selective alkene isomerization, we focused our attention towards our PC_{NHC}P pincer ligands, which are an excellent platform for coordinating earth-abundant metals and for supporting unusual reactivity.¹⁷ Using a similar synthetic strategy to the one developed recently for our iron complexes,^{17c} we were able to obtain the corresponding $[(PC_{NHC}P)CoCl_2]$ complex **1**, which was used without further purification in the next step (Scheme 1). Addition of potassium graphite (KC₈; 1.01 equiv.) to the crude reaction mixture containing complex **1** resulted in a clean one-electron reduction of **1** to yield the diamagnetic cobalt(I) complex [(PC_{NHC}P)CoCl] (2). Addition of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBAr₄^F) to a solution of **2** in diethyl ether (Et₂O) resulted in facile abstraction of the chloride to furnish the cationic cobalt(I) dinitrogen complex 3, which is a

the cationic cobalt(I) dinitrogen complex **3**, which is a dimer in the solid state (**Figure 2**). Alternatively, addition of 1.01 equiv. of methyl-magnesium bromide (MeMgBr) to complex **2** furnishes the diamagnetic cobalt(I) methyl species (**4**) in excellent yields (**Scheme 1**).

According to X-ray crystallography (**Figure 2**), complexes **2–4** all feature a cobalt metal center in a square planar geometry. The Co–C1 carbene bond distances of 1.769(8) Å (**2**), 1.805(6) Å (**3**), and 1.781(7) Å (**4**), are quite short but comparable to other cobalt pincer complexes that feature a carbene donor.¹⁸ The Co–C1 distance in complex **3**, however, is slightly elongated compared to those in **2** and **4** due to competitive π -backbonding with the N₂ ligand. Although dimeric, the two Co(I) centers in complex **3** do not activate the N–N bond (1.174(7) Å) to a great extent.¹⁹ Overall, the spectroscopic and structural data



Figure 2. Solid state structures of (A) [(PC_{NHC}P)CoCl] (**2**), (B) [((PC_{NHC}P)Co)₂-μ-N₂][BAr₄^F]₂ (**3**) and (C) [(PC_{NHC}P)CoMe] (**4**). Thermal ellipsoids are shown at the 30% probability level. Counter anions and co-crystallized solvent molecules are omitted for clarity. Complex **3** has been truncated to the monomer for comparison.

confirm the formation of well-defined Co(I) complexes with nearly identical bond metrics (**Table S2**). Because these complexes are iso-structural, we embarked on a comparative study into allyl ether isomerization.

Allyl ether isomerization with iso-structural Cobalt(I) $\mathsf{PC}_{\mathsf{NHC}}\mathsf{P}$ pincer complexes.

Having fully characterized complexes **3** and **4**, their activity in the isomerization of terminal allyl ethers was investigated. We decided to focus on allyl ethers because (i) the corresponding enol ethers could be used in subsequent reactions such as the Coates-Claisen rearrangement²⁰ and (ii) to the best of our knowledge, there has only been one report on the Zselective isomerization of allyl ethers with earthabundant metals (Figure 1A).^{8h} In this report, however, Chen and co-workers used stoichiometric amounts of Me₃NFPy·OTf and Me₂SiH₂ to facilitate the isomerization, severely limiting scalability and sustainability. In addition, the iso-structural nature of our complexes also allows us to establish important structure-function relationships that could affect the stereoselectivity of the isomerization reaction.

Using allylbenzyl ether as benchmark substrate, it was quickly established that the optimal conditions for positional alkene isomerization are: 60 °C temperature with 1 mol% catalyst **3** and benzene-d₆ as solvent (**Table S1**). Under these conditions, complete conversion of allylbenzyl ether to the corresponding enol ether was observed. Interestingly, the *Z*-isomer was predominantly detected in the reaction mixture (E/Z = 1:3). Gratifyingly, these conditions could also be applied to the isomerization of electronically and sterically differentiated allyl ethers (**Table 1**), all giving roughly the same E/Z ratio favoring the *Z*-isomer. For example, under the optimized conditions, allylbenzyl ethers containing

both electron donating (-OMe) and electron withdrawing (-CF₃) groups could be efficiently isomerized to their corresponding enol ethers 5d and **5f**, with stereoselectivities $\geq 1:3$ (*E*/*Z*). Ortho substituted allylbenzyl ethers are also well tolerated, with little to no influence of the substitution pattern on the yield or the stereoselectivity of the reaction (**Table 1**: **5c** and **5e**). Linear aliphatic allvl ethers were isomerized selectively with also similar stereoselectivities as their benzyl counterparts (Table 1; 5i-5j). Since di-substituted alkenes are not isomerized, selectivity is obtained when several double bonds are present in the substrate (Table 1; 5k and 5l). Furthermore, these enol ethers could subsequently be used for the Coates-Claisen rearrangement as beautifully illustrated by Marek and co-workers.²⁰ Sensitive functional groups such as epoxides and allyl silyl ethers are tolerated as well (Table 1: 5n-5s). Moreover, allyl ethers bearing natural product-derived substituents, such as bornane (5q and 5r) and menthol (5t) are also isomerized efficiently. Overall, catalyst 3 exhibits a wide substrate scope and operates under mild conditions (60 °C, 5-16 hours) and an inert atmosphere. Interestingly, while catalyst **4** presents a similar substrate scope (**Table 1**), the observed stereoselectivity is opposite to that of catalyst **3**, whereby now the *E*-isomer is observed as the major product. Although the E/Zratios are modest, typically 2:1, the reversal of selectivity is remarkable, considering that the only structural change is replacement of the $\ensuremath{-N_2}$ for a methyl (-Me) substituent on the cobalt metal center.

To elucidate the mechanism of this reaction, we performed a series of deuterium labeling experiments. For synthetic simplicity,²¹ we performed a cross-over experiment with 3,3-d₂-dec-1-ene and 4-allyl-1,2-dimethoxybenzene. Analysis of the reaction mixture revealed no scrambling of the deuterium label

Table 1. Isomerization of allyl ethers catalyzed by complexes 3 and 4.ª



^aReactions were performed with 1-5 mol % catalyst **3**, and 0.30 mmol alkene in 400 μ L benzene- d_6 for 5-16 hours at 60 °C. ^bReactions were performed with 2-5 mol % catalyst **4**, and 0.15 mmol alkene in 400 μ L toluene- d_8 for 3-16 hours at 80 °C. Yields and stereoselectivities were determined by ¹H and ¹³C NMR spectroscopy.

for either catalyst (Figures S91-S94). The absence of any scrambling is highly indicative of an allyl-type mechanism. Moreover, when $1,1-d_2$ -dec-1-ene was used as substrate and complex 4 as catalyst, deuterium was incorporated exclusively at the 1,3position, not only supporting an allyl-type mechanism, but also indicating that the isomerization process is reversible (Figures S95-S100). In contrast, when using catalyst 3, deuterium was only incorporated marginally, indicating limited reversibility of the isomerization. Additionally, monitoring the isomerization reaction as a function of time showed that for both catalysts **3** and **4** the E/Z ratios remained constant, indicating their formation is kinetically controlled. despite the E-isomer being thermodynamically favored (vide supra).

Finally, a radical-type mechanism was ruled out because the isomerization of allylbenzyl ether proceeded smoothly in the presence of known radical scavengers such as 9,10-dihydroanthracene, xanthene, or 1,1-diphenyl-ethylene (**Figures S101– S112**).⁸ Other radical scavengers, such as di-*tert*butylhydroxytoluene or TEMPO, were not used as they interact with the metal center, producing catalytically inactive complexes.^{7b} Furthermore, for substrates exhibiting a 1,6-diene motif, no cyclization was observed, as shown in **Table 1** (**5k** and **5l**), ruling out a radical mechanism as well. Overall, these experimental studies are consistent with an allyl-type mechanism for allyl ether isomerization, where the observed stereoselectivity is catalyst-dependent and does not result from ready interconversion of one isomer into the other.

Computational Mechanistic Investigations.

To gain more insight into the origin of stereoselectivity and to identify the reasons for the reversal of stereoselectivity, we used density functional theory (DFT) calculations to characterize the relevant stationary points and transition-state structures along the reaction pathway. To alleviate computational complexity, calculations were performed with a truncated model of the catalyst (**Figure 3–6**), in which the *tert*-butyl substituents on the backbone were replaced with methyl groups (see Supporting Information for computational details). For our computational studies, the X-ray structures of complexes **3** and **4** served as a benchmark, following

which we selected the PBE0-D3BJ/def2-SVP combination for C, H, N, O and the PBE0-D3BJ/def2-TZVP level of theory for Co. The optimized geometries of 3 and 4 are shown in Figure S116, and the structural parameters show calculated good agreement with those determined by X-ray crystallography (Table S4).



Figure 3. Calculated free energy profiles (ΔG) in kcal/mol for the isomerization of allylbenzyl ether with complex **3**. See the supporting information for more computational details.

We began our mechanistic evaluation by studying the isomerization of allylbenzyl ether with complex 3 (Figure 3). Starting from complex 3, coordination of the alkene is energetically uphill by 9.9 kcal/mol. Upon coordination of the allyl ether, the geometry around the cobalt metal center changes from square planar to distorted square pyramidal, which mainly results in an increase of the Co–N (N₂) bond distance from 1.784 Å in **Co-N**₂ to 1.865 Å in **N**₂-**Int2**, due to decreased π -backbonding when N₂ moves from an equatorial to an axial position. Thereafter, oxidative addition occurs via one of two distinct transitionstates (N₂-TS2-E = 38.8 kcal/mol; N₂-TS2-Z = 36.1 kcal/mol), leading to either the *E*- or *Z*-isomer of the secondary cobalt alkyl complex N₂-Int3-E (23.3) kcal/mol) or N₂-Int3-Z (27.8 kcal/mol), respectively. As evident from the transition-state energies, the Zisomer is favored by ca. 2.7 kcal/mol, which is in agreement with our experimental data. However, the calculated transition-state barriers of 38.8 and 36.1

kcal/mol are too high in energy to be accessible under the experimental reaction conditions. Even if these were accessible, migration of the cobalt metal center from the internal to the terminal carbon via a π -allyl intermediate results in loss of the N₂ ligand, changing the overall mechanistic and energetic landscape. As a result, an alternative pathway was evaluated, whereby N₂ dissociates prior to coordination of the alkene (**Figure 4**).

Starting from Co-N₂, dissociation of N₂ results in the formation of a T-shaped cobalt complex ($Co-\Box$),²² which is energetically uphill by 24.2 kcal/mol. Coordination of the allyl ether stabilizes this coordinatively unsaturated species by 18.2 kcal/mol, through formation of a cobalt-alkene complex (Int2). Alternatively, N₂ could also dissociate from N₂-Int2, (Figure 3), leading to the coordinated alkene complex Int2 with an overall stabilization of 3.9 kcal/mol, providing a crossover between the N₂-coordinated (Figure 3) and de-coordinated pathways (Figure 4). From this square planar intermediate (Int2), oxidative addition occurs with transition-state barriers of 23.9 or 21.7 kcal/mol for the E- and Zisomers respectively. Thus, compared to the previously calculated transition-state barriers of 38.8 kcal/mol and 36.1 kcal/mol (vide supra), dissociation of the N₂ ligand prior to oxidative addition lowers the respective barriers by approximately 14.8 kcal/mol for the *E*-isomer and 14.4 kcal/mol for the *Z*-isomer. In both scenarios, the stereoselectivity of the oxidative addition is in accordance with our experimental results (Figure 4). The difference is, however, that dissociation of the additional N₂-ligand allows for formation of the π -allyl interaction that stabilizes the transition-state, resulting in overall lowering of the energy barrier (Figure 5). As a result, when N_2 dissociates, the product of C-H bond activation is not the secondary-alkyl hydride N_2 -Int3E/Z, but rather the more stable π -allyl hydride cobalt complex Int3-E/Z with a preferred Z-geometry of the coordinated η^3 -allyl (**Figures 3–5**). From the π -allyl intermediate **Int3-***E***/Z**, the coordinated allyl ether rearranges via transition states **TS3-**E/Z to the η^{1-} allyl cobalt complexes Int4-E/Z, respectively.

From these intermediates, two distinct pathways are possible. In the first pathway (**Figure4**; blue and red traces), the η^1 -allyl isomers **Int4-***E*/*Z* revert to their η^3 -allyl counterparts, effectively accomplishing a 180° rotation of the allyl ether fragment (**Figure 4**; **Int3-***E*/*Z* vs. **Int5-***E*/*Z*). Interestingly, upon rotation, the *E*-isomer of the allyl ether fragment becomes more stable than its *Z*-congener (*E*; 12.5 kcal/mol vs. *Z*; 17.3 kcal/mol). This energetic difference is preserved in the transition states for reductive elimination (**TS**-**5***E*/*Z*), leading to the enol ethers **Int6-***E*/*Z*. However, our experimental results demonstrate that allyl ether isomerization with complex **3** is not reversible (*vide supra*), signifying that the stereoselectivity is determined at the first oxidative additions step (**Figure 4**; **TS2-***E*/*Z*), for which the *Z*-isomer is preferred by 2.2 kcal/mol. Furthermore, this mechanistic pathway also reveals that for both the *E*-and *Z*-isomers migration of the cobalt metal center from an η^3 - to an η^1 -allyl intermediate has the highest-energy transition-state barrier (**Figure 4**, **TS3-***E*=28.6 kcal/mol; **TS3-***Z*=27.4 kcal/mol), where again the Z-isomer is preferred by 1.2 kcal/mol.

Alternatively, in the second pathway (**Figure 4**; green trace), the reductive elimination occurs immediately from the η^1 -allyl intermediates **Int4-***E*/*Z* to produce the corresponding enol ethers. The reductive elimination occurs with transition-state barriers of 27.2 (*E*) and 25.8 (*Z*) kcal/mol. These computational data thus suggest that regardless of the overall chosen pathway, formation of the *Z*-isomer is preferred, either by $\Delta\Delta G^{\ddagger}$ = 2.2 kcal/mol (pathway 1) or by $\Delta\Delta G^{\ddagger}$ = 1.4 kcal/mol (pathway 2),²³ which is in good qualitative agreement with the experimentally observed preference for the *Z*-isomer (**Table 1**).

At this point, we wish to emphasize that the selectivity corresponds to differences in energies on the order of single kilocalories per mole (**Figure 4**), that are well within the error of DFT. However, it is our aim to provide qualitative chemical insight into the isomerization process, rather than predicting the

exact energy of each stationary point and transitionstate. Notwithstanding, the obtained computational results are in good agreement with the experimental observations, with energies that are within the realm of our experimental conditions. Furthermore, they provide important insight into how the observed Zstereoselectivity results from loss of the N₂ ligand enabling the initial formation of an η^{3-} allyl cobalt intermediate with a preferred Z-geometry. This Zselectivity is preserved throughout the reaction either through (i) a series of ether rotations followed by reductive elimination or (ii) direct reductive elimination of the enol ether from a η^1 -allyl intermediate. Although the Z-enol ether is thermodynamically only marginally more stable than the *E*-isomer. The *Z*-isomer is also the kinetic product of the reaction whose formation is dictated by the initial oxidative addition, which is in good agreement with our experimental observations and our deuterium labeling experiments (vide supra).

Thus far, our computational studies revealed the importance of dissociation of the N₂-ligand to enable the observed Z-selectivity. For cobalt complex **4**, however, such dissociation is impossible. Nevertheless, reversible migration of the methyl substituent to the carbene carbon atom (C_{NHC}) would generate a vacant coordination site, enabling the formation of an η^3 -allyl intermediate in an analogous manner to N₂ dissociation.



Figure 4. Calculated free energy profiles (ΔG) in kcal/mol for the isomerization of allylbenzyl ether with complex **3** after N₂ dissociation. See the supporting information for more computational details.



Figure 5. Optimized geometries of the calculated transitions states **N2-TS2-***E* (A), **TS2-***E*, and **TS2-***Z* on the singlet potential energy surface. See the supplemental information for more computational details.

As such, the $PC_{NHC}P$ ligand would hereby be considered non-innocent. Such migrations, although rare, have been reported in the literature.²⁴ For example, Fryzuk, Green and co-workers reported the migration of an ethyl-fragment from nickel to the NHC-carbon in a similar $PC_{NHC}P$ pincer ligand.²⁵ Similarly, Bercaw and co-workers reported the reversible migration of a benzyl-substituent from zirconium to an NHC-carbon.²⁶ Supporting these earlier observations, our computational studies indicate that such a mechanism is indeed the lowest energy pathway towards isomerization with complex **4** (**Figure 6**). The isomerization process starts with coordination of the allyl ether to the cobalt metal center, which is energetically uphill by 11.2 kcal/mol (**Figure 6**; **Me-Int2**). Hereafter, we have identified two potential pathways: The first is a lower-energy pathway that involves migration of the methyl substituent from the cobalt metal center to the NHC carbon of the ligand with a transition state of 21.7 kcal/mol (**Figure 6**; **Me-TS2**). The second pathway involves oxidative addition of the allylic C–H bond with transition-state barriers of 37.2 and 35.2 kcal/mol leading to the *E*- and *Z*- isomers of the secondary cobalt alkyl complex, respectively (See Supporting Information; **Figure S117**).



Figure 6. Calculated free energy profiles (ΔG) in kcal/mol for the isomerization of allylbenzyl ether with complex **4**. See the supporting information for more computational details.

E-Isomer

This process is akin to that calculated for the cationic intermediate **N₂-Int2** and is likewise too high in energy to be feasible under the experimental reaction conditions. In addition, despite extensive efforts, we were unable to find the π -allyl transition-state allowing the η^3 -allyl to η^1 -allyl migration and enabling the cobalt metal center to move from the internal to the terminal carbon of the allyl ether. The reason is that the methyl ligand not only provides a steric barrier, but also occupies one of the d-orbitals that is necessary for π -allyl formation. As a result, the methyl substituent must migrate from the cobalt to the NHC carbon to generate a vacant coordination site.

Returning to the first pathway, after migration of the methyl to the NHC (Figure 6; Me-Int3), oxidative addition of the allylic C-H bond readily occurs to produce the *E*- and *Z*-isomers of **Me-Int4** with transition-state barriers of 18.1 (E) and 23.1 (Z) kcal/mol. With the methyl group out of the way, isomerization occurs via a similar mechanism to that calculated for complex **3**. From the π -allyl intermediate **Me-Int4-***E***/Z**, the coordinated allyl ether rearranges via an η^{3-} to η^{1-} to η^{3-} interaction to effectively accomplish a 180° rotation of the allyl ether fragment (Figure 6; Me-Int4- $E/Z \rightarrow$ Me-Int6-E/Z). For both the *E*- and *Z*-isomers, isomerization to the η^{1} allyl intermediate (Me-Int5-E/Z) is energetically the most demanding, with the *E*-isomer pathway being slightly lower in energy (Figure 5; compare Me-TS4-*E*: 26.6 kcal/mol vs. **Me-TS4-Z**: 27.3 kcal/mol). Akin to complex **3**, direct reductive elimination from the η^{1} allyl intermediate Me-Int5-E/Z to the enol ether intermediate **Me-Int6-***E***/Z** is also possible, with transition-states barriers that are nearly identical in energy (Figure 6; TSRE-E: 30.7 kcal/mol; TSRE-Z: 31.1 kcal/mol). With the isomerization accomplished, the methyl-substituent now migrates back from the NHC carbon to the cobalt metal center via a transitionstate with a barrier of 22.8 kcal/mol (E) or 23.7 kcal/mol (Z), completing the isomerization of the allyl ether to the enol ether (Figure 6; Me-TS7-*E*/*Z*).

Compared to complex **3**, there is one notable difference in the calculated isomerization process, besides the difference in mechanism. Namely, the transition state towards oxidative addition (**Me-TS3**) has the opposite stereoselectivity. Whereas for complex **3**, the *Z*-isomer is lower in energy, for complex **4** the *E*-isomer is lowest in energy by about 3.0 kcal/mol (Compare **TS2** and **Me-TS3**; **Figures 4** and **5**). The reversal is most likely due to the increase steric congestion around the metal center, even when the methyl has migrated to the NHC carbon. As a result, the *E*-isomer pathway is preferred across the entire reaction coordinate (**Figure 6**). This could explain the observed experimental differences in stereoselectivity, whereby our deuterium labeling

studies indicate that allyl ether isomerization catalyzed by complex **4** is reversible (**Figures S98–S100**). As a result, the thermodynamically most stable product is expected. Indeed, here also the *E*-isomer is preferred by about 2.5 kcal/mol (**Figure 6**; compare **Me-Int8-***E***/Z**). Although these differences are within the error of DFT, these values nonetheless indicate that both isomers are expected at almost equal quantities, with a slight preference for the *E*-isomer, which agrees with our experimental data for this complex. More importantly, however, is the first demonstration of a reversible 1,2-methyl migration that is relevant for catalysis, which to the best of our knowledge is unprecedented, and yet has large consequences for the isomerization of allyl ethers.

SUMMARY & CONCLUSIONS

In summary, we reported the first synthesis of a variety of cobalt $PC_{NHC}P$ pincer complexes that are active for the isomerization of sterically and electronically differentiated allyl ethers. The reaction occurs between 60–100 °C and shows preferences for either the Z-isomer (complex 3) or E-isomer (complex 4). Mechanistic and computational studies showed that the reaction occurs via an allyl-type mechanism. where the stereochemistry is determined by (i) the ability to form a stable π -allyl intermediate and (ii) the steric crowding around this π -allyl intermediate. As a result, for complex **3** dissociation of N₂ is necessary to allow the formation of a η^3 - π -allyl intermediate that prefers the *Z*-isomer. In contrast, for complex **4**, such dissociation is not possible and allyl ether isomerization proceeds via an unprecedented reversible migration of the methyl substituent from the cobalt metal center to the NHC carbon, which enables the formation of the π -allyl intermediate with a preferred *E*-geometry. Overall, the isomerization occurs with good yields and the computational studies provide ample benchmarks for optimized ligand designs for Z-selective olefin isomerization.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at the ACS website.

Crystal data (CIF) xyz-coordinate files (ZIP) Synthetic procedures, characterization data, catalysis, and computational studies (PDF)

AUTHOR CONTRIBUTIONs

Conceptualization, S.G., R.G.P., and G.d.R.; Methodology, S.G., S.R., T.S.M., R.R., R.G.P. and G.d.R.; Investigation, S.G., S.R., K.M.P., R.G.P. and G.d.R.; Writing – Original Draft, R.G.P. and G.d.R.; Visualization, K.M.P., R.G.P., and G.d.R.; Computation: K.M.P. and R.G.P.; Funding Acquisition, R.G.P. and G.d.R.; Resources, R.G.P., N.F. and L.J.W.S.; Supervision, R.G.P. and G.d.R.

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Notes

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