Distinctive Reaction Pathways at Base Metals in High-Spin Organometallic Catalysts

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CONSPECTUS: Inexpensive "base" metals are more affordable and sustainable than precious metals and also offer opportunities to discover new mechanisms for selective catalytic reactions. Base metal complexes can have high-spin electronic configurations that are rare in precious metal complexes. This Account describes some concepts relevant to high-spin organometallic complexes, focusing on our recent work with β-diketiminate complexes of iron and cobalt. Even though high-spin organometallic complexes have some unfamiliar spectroscopic properties, they can be studied using NMR spectroscopy as well as techniques that focus on the magnetism brought about by the unpaired electrons.

Understanding the mechanisms of reactions using these complexes can be complicated, because complexes with a high-spin electronic configuration may need to change spin states to avoid high barriers for reaction. These spin-state changes can be rapid, and the ability of an excited spin state to "cut through" the barrier for a reaction can lead to spin acceleration. These concepts, originally developed by Poli, Shaik, Schwarz, and Harvey, are applied here to the fundamental organometallic reaction of β-hydride elimination (BHE). Experimentally validated density-functional calculations show spin acceleration in BHE using three-coordinate iron(II) and cobalt(II) complexes. A square-planar transition state is particularly beneficial for accelerating BHE when a high-spin iron(II) complex goes from an $S = 2$ ground state to an $S = 1$ transition state or when a high-spin cobalt(II) complex goes from an $S = 3/2$ ground state to an $S = 1/2$ transition state. The relative energies of the spin states can be controlled with the choice of the supporting ligand. Using an appropriate ligand, isomerization of 1-alkenes to their Z-2 isomers can be catalyzed in high yields using the cobalt(II) alkyl complexes as catalysts. Though an earlier paper attributed the regioselectivity and stereoselectivity to the preferred geometry of the BHE step, the results of isotope labeling experiments suggest that the selectivity may actually come from the alkene exchange step (again with spin acceleration). In general, the use of multiple intersecting spin states is envisioned as a profitable strategy for bringing about low reaction barriers and high selectivity in catalytic reactions. This effort requires high-accuracy computational models as well as ligand design that gives nearby spin states with appropriate geometries.
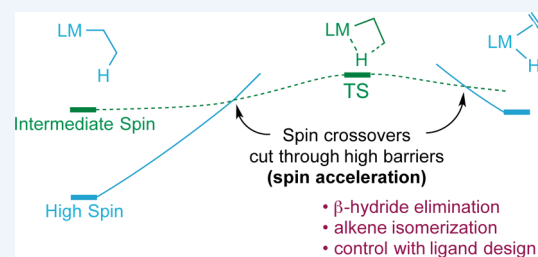
FIRST-ROW ORGANOMETALLICS FOR SUSTAINABLE CHEMISTRY

Catalysts containing "platinum group" metals ($4d$ and $5d$ transition metals in groups 8, 9, and 10; Figure 1) play a very important role in organometallic chemistry, particularly in hydrocarbon transformations and strong bond activation.[1−3] Part of the popularity of these metals comes from the relative stability and lower ligand lability of their complexes, and the ability to characterize diamagnetic complexes in solution using NMR spectroscopy. Most importantly, complexes of these metals have exceptional catalytic abilities. Prominent examples include alkene metathesis with ruthenium catalysts,[4] cross-coupling reactions with palladium catalysts,[5] C−H activation reactions with iridium and rhodium catalysts,[6] and hydrosilylation with platinum catalysts.[7]

However, the current dominance of platinum group metals is not sustainable for a number of reasons.[8] (1) The abundance of these metals on Earth is low, and though the metals may be recycled, some is inevitably lost. In polymerizations based on alkene metathesis ("ROMP") or hydrosilylation, the catalyst is typically left in the reaction product.[7] (2) The cost is high (though ruthenium is somewhat less expensive than the others).[9] (3) Because of the toxicity of heavy metals, levels of platinum group metals in pharmaceuticals are limited to 10 ppm.[10] This contrasts with iron, for which simple salts are common nutritional supplements. (4) Production and separation of precious metals is more energy-consuming for platinum-group metals than for Fe, Co, and Ni.[11]

These considerations have motivated chemists to replace precious metals with base metals on the basis of periodic similarities (Figure 1). In addition to substituting for their precious-metal analogues, one could even hope that the base-metal catalysts would give novel reactivity and selectivity to

Fe	Co	Ni
Ru	Rh	Pd
Os	Ir	Pt

Figure 1. "Platinum group metals" are shown in orange, and the corresponding more sustainable "base metals" are shown in green.

enable the development of new processes. However, characterization of catalysts with first-row metals is more challenging because the weak ligand field of many first-row complexes often gives paramagnetic complexes ($S > 0$). In addition to the characterization difficulties, there has been a perception that high-spin complexes as "metalloradicals" inevitably lead to free radicals and decomposition. Thus, many studies with base metals have been done using low-spin, diamagnetic carbonyl and cyanide complexes. For example, it has long been known that $Co(CN)_5^{3-}$ catalyzes hydrogenation and $Co_2(CO)_8$ catalyzes hydroformylation, but each cobalt catalyst has been supplanted by precious-metal catalysts.[1,2]

Recent developments have rejuvenated the prospects for paramagnetic Fe, Co, and Ni complexes as active catalysts. For example, chemists have discovered base metal-catalyzed C−C coupling reactions where the only available ligands are weak-field halides, O-donors (e.g., acac, acetylacetonate), solvent, or additives (e.g., NMP, N-methylpyrrolidinone).[12−15] Assuming that the weak ligand field in these complexes would cause the organometallic species along the catalytic cycle to have high-spin electronic configurations, this implies that high-spin complexes of first-row metals are active for catalysis. Though studies in the 1970s suggested that high-spin first-row metals would give radical chemistry and unselective reactions,[16] many of the recent catalytic reactions have exquisite selectivity. However, the coordination environment of the metal is often unclear in the active catalysts. This ambiguity hinders mechanistic understanding that is needed for rational advances in catalytic activity and selectivity. More generally, it is not understood in which cases a high-spin catalyst may offer benefits, and there are few conceptual models for thinking about their reactivity. New conceptual work in this area is emerging, including Shaik's exchange-enhanced reactivity.[17]

■ PARAMAGNETIC ORGANOMETALLIC COMPLEXES: MISCONCEPTIONS, DIFFICULTIES, AND OPPORTUNITIES

First, it is useful to address some common misconceptions by stating some facts that are not part of the core conventional wisdom of organometallic chemistry. First, *weak-field ligands can be strong-binding ligands*. Organometallic chemists often assume that stronger ligand fields correspond with thermodynamically strong bonds, because the ligand field orbitals include the antibonding counterparts to the σ-bonding orbitals shared by the metal and the donor atom. However, this is not always the case, because many π-donor ligands (e.g., thiolates, amides) bind strongly to metals yet give high-spin complexes because the σ-nonbonding orbitals are pushed up in energy by the π interactions. Because all of the ligand-field orbitals are close in energy, the small ligand-field splitting does not overcome the pairing energy. Second, *NMR spectra are useful for paramagnetic compounds*. The presence of unpaired spin has two major influences on NMR signals. The first is shifting of the

resonances; however, with the sensitivity and fast electronics of modern NMR spectrometers, it is possible to expand the sweep width to 500 or 1000 ppm. With short acquisition times, dozens of scans can be accumulated to enhance the intensity. The second is an increase in broadness, which is most problematic in systems with slow electronic relaxation (e.g., $S = 1/2$) that are often NMR silent. However, with $S > 1/2$ systems having low-lying excited states (which include iron and cobalt complexes that are promising for catalysis, for reasons explained below), spin−orbit coupling gives fast electronic relaxation and relatively sharp signals in NMR spectra. In these cases, ^1H NMR spectra of high-spin complexes can be integrated, enabling studies on kinetics, dynamics, and purity using NMR spectroscopy. There are well-established methods for gaining information about structure, dynamics, and electronic structure in paramagnetic NMR spectroscopy,[18] though these opportunities have rarely been realized with organometallic compounds. More generally, *paramagnetic complexes are particularly receptive to spectroscopic study*. They typically have intense colors, and the visible absorption bands can be correlated with computational results using time-dependent density functional theory (TD-DFT).[19] Magnetic susceptibility and magnetic circular dichroism (MCD) can correlate the magnetism to ligand-field splitting. Electron paramagnetic resonance (EPR) spectroscopy gives detailed electronic structure information for systems with noninteger spin ($S = 1/2, 3/2, 5/2$).

However, there are challenges. Computational investigations are more complicated in paramagnetic systems, because the accuracy of DFT calculations on high-multiplicity species tends to be very functional-dependent,[19] and also because first-row metals often have multiple spin states with similar energies. Because the difference between the spin state energies is geometry-dependent, geometric changes during a reaction may lead to crossing of the potential-energy surfaces. Therefore, *consideration of a reaction pathway requires the characterization of multiple potential energy surfaces*. Though the added surfaces complicate our conceptual understanding of a reaction, the advantage of multiple potential energy surfaces is that molecules can switch spin states to avoid high barriers.[20] Figure 2 illustrates how a large barrier for a high-spin complex (solid line) may be avoided when another spin state (dotted line) cuts through the barrier. This situation has been termed "spin acceleration"[21] and is a subset of "two-state reactivity".[22]

The red points in Figure 2 represent geometries at which the two spin states have identical energies. In the multidimensional potential energy surface, there are many such crossing points, but the lowest ones are referred to as minimum-energy crossing points (MECPs). If the MECP lies above the transition state of the excited-state potential-energy surface, then spin crossover creates an extra barrier ("spin blocking"). If the MECP energy lies below those of both transition states (as in Figure 2), there is no additional hindrance to the reaction from spin crossover because strong spin−orbit coupling relaxes the selection rule
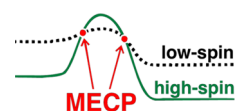

Figure 2. Spin acceleration in a high-spin complex. In red are indicated the "minimum energy crossing points" (MECP) where an electron spin flips to change the spin state.

against spin flipping in transition-metal complexes.[20] To date, there are few examples where spin crossover has been demonstrated or postulated in catalytic organometallic reactions.[20,23] This Account describes research (focusing on work from my research group and collaborators) that explains how spin acceleration provides a framework for beginning to understand the pathways and selectivity for the reactions of certain high-spin organometallic complexes.

β-DIKETIMINATE COMPLEXES AS A PLATFORM FOR SYSTEMATIC STUDY OF HIGH-SPIN FE AND CO

β-Diketiminate ligands (Figure 3) are σ and π donors and therefore give high-spin complexes. In the hundreds of diketiminate-supported iron and cobalt complexes we have reported, the vast majority are high spin, and the only ones with low-spin electronic configurations are those with CO or isocyanide ligands.[24] The primary reason for the high-spin electronic configuration is the low coordination number at the metal center, which comes from bulky groups in the ortho positions of the N-aryl substituents. The β-diketiminate ligand set also has a number of other advantages, including steric and electronic tunability, ease of synthesis, and ease of incorporation into complexes. These are described in detail elsewhere.[24]

Despite the "18-electron rule" of organometallic chemistry, it is possible to isolate high-spin iron(II) and cobalt(II) alkyl complexes that have only 12 or 13 electrons shared by the metal, considering the diketiminate as a 4-electron (LX) donor. Even though alkyls are considered strong-field ligands, the electronic properties at the metal are dominated by the diketiminate, and the complexes have high-spin configurations at the metal with 4 and 3 unpaired electrons at the metal. These have served as a useful platform for the exploration of well-characterized high-spin organometallic systems, although the principles that emerge are expected to be more general.[24]

β-HYDRIDE ELIMINATION THROUGH SPIN ACCELERATION

β-Hydride elimination (BHE) is one of the fundamental reactions of organometallic chemistry (Figure 4). Depending on the application, BHE may be desired or detrimental. For example, alkene isomerization and the Heck reaction involve BHE as a fundamental step.[1] In other cases like polymerization and cross-coupling reactions, BHE is undesired.[5,25] Thus, control over BHE is crucial. Interestingly, some high-spin organometallic complexes have been described as "BHE-resistant", such as $[MnEt_4]^{2-}$ and $Tp^{R2}FeEt$ (Tp = tris-(pyrazolyl)borate ligand; R_2 = iPr$_2$, tBu/Me).[26,27] The rationale for the BHE resistance has been that a high-spin complex with 5 or more d electrons has no empty d orbital to accept the two electrons from the β-hydrogen that becomes the hydride.[28]

Figure 3. β-Diketiminate ligands, demonstrating the notation for R and R′ substituents.
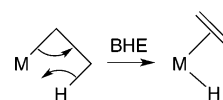
Figure 4. β-Hydride elimination.

We showed that BHE could take place from iron(II) diketiminate complexes, even though they have a high-spin electronic configuration.[29] I will refer to this as spin-forbidden BHE.[30] Key evidence for BHE in these systems included the primary H/D kinetic isotope effect on the rate of alkyl chain walking.[31] We recently used DFT calculations (using truncated diketiminate ligands) to test electronic structure changes during this mechanism.[32] Figure 5 shows that the quintet ground state (high-spin d^6, 4 unpaired electrons, $S = 2$) of $L^{trunc}FeEt$ has a high free energy barrier of 30 kcal/mol for BHE, but that the triplet (intermediate-spin d^6, 2 unpaired electrons, $S = 1$) state has a much lower-energy transition state (TS) that is only 19 kcal/mol above the quintet ground state. The molecule can change from the quintet to the triplet state (flipping one electron spin) at a MECP with a geometry similar to that of the triplet ground state. The triplet excited state is well-suited for BHE: it has a β-agostic interaction in the alkyl complex, and there is a barrier of only 5 kcal/mol for BHE along the triplet potential energy surface. The barrier calculated with full-ligand models was 21 kcal/mol, which compares well to the value of 23 kcal/mol determined through kinetic studies.[31]

Why do the diketiminate complexes undergo a spin flip while the BHE-resistant complexes do not? We evaluated this question by comparing the results described above to computations on the iron(II) tris(pyrazolyl)borate complex TpFeEt, a truncated model of a BHE-resistant complex described by Theopold.[26] The computations showed that the TpFe system also undergoes spin acceleration but even with this assistance requires a high calculated barrier of 32 kcal/mol for BHE.[32] The reason for the BHE resistance became clear upon examining the geometries of the transition states (Figure 6). In each complex, the transition state and the MECP (as well as the triplet excited state) had a square-planar geometry, considering the incipient M–H bond as one of the ligands. However, the Tp complex has difficulties reaching this square-planar transition state because it must partially dissociate a ligand, which is enthalpically unfavorable. On the other hand, in a diketiminate complex with a bite angle of 95° and steric
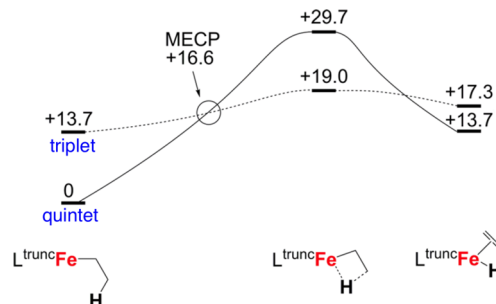
Figure 5. Triplet and quintet potential energy surfaces (PES) for BHE calculated using a simplified β-diketiminate ligand $L^{trunc} = C_3N_2H_5^-$ as described in ref 32. The triplet surface is the dashed line, and the quintet surface is the solid line. The surfaces cross at the indicated MECP, and the triplet transition state is lower than the quartet transition state (spin acceleration). Relative Gibbs free energies are given in kcal/mol.
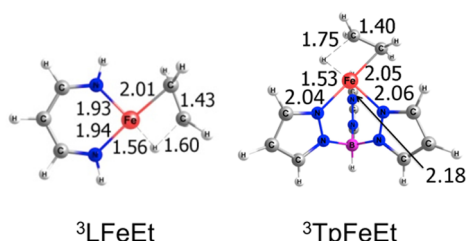
Figure 6. Triplet transition states for BHE as calculated for simplified β-diketiminate complexes that do undergo BHE and for simplified tris(pyrazolyl)borate (Tp) complexes that do not undergo BHE.[32] Bond distances (in Å) are indicated; note that in the Tp complex, one of the Fe−N bonds is lengthened, which is destabilizing and raises the activation barrier for the reaction.

pressure above and below the ligand plane, this square-planar geometry is enforced by the ligand.

This highlights several important aspects of spin acceleration[21] that have the potential to improve a broader range of reactions of base−metal complexes. First, the ability of a high-spin complex to benefit from spin acceleration is dependent on the geometry of the complex. Spin acceleration requires a specific type of spin-state change; in this case, changing to the triplet excited state empties the orbital on the metal that needs to accept electron density during the BHE reaction. Second, the geometric rearrangement between the equilibrium geometries should not be too drastic; otherwise, the energetically costly distortions would give a high-energy MECP. In the diketiminate complexes described above, the MECP is lower in energy than the triplet transition state, and thus, crossover does not limit the rate. Third, computational analysis is an essential part of the understanding of the reaction because the barrier-crossing state may be undetectable. In the case of BHE discussed here, all of the observable species (starting materials and products) are quintets. According to our computational model, the triplet state is accessed only at higher points on the reaction coordinate and not at any stable minimum on any potential energy surface. Thus, the triplet has no significant population despite its major influence on the reaction.

How then can one evaluate the potential for spin acceleration? Recall that in our computational study,[32] the ground-state geometry of the triplet state had a geometry similar to the MECP for BHE and actually had an agostic interaction that resembles incipient BHE. The similarities in geometry are not surprising, because the energy of the MECP was similar to that of the optimized triplet geometry. This implies that geometry optimization of excited states can (at least in favorable cases) give hints about the pathways favored by spin acceleration.

Spin acceleration involves hopping between potential energy surfaces, and it thus requires an electronic excited state with relatively low energy. Thus, one expects spin acceleration in systems with closely spaced spin states. High-spin complexes with extremely weak ligand fields may not be suitable for spin acceleration if the reactive intermediate or low spin excited states are much higher in energy. This concept has been emphasized by Cundari and Wolczanski in terms of the density of states[33] and by Shaik in analysis of reactive iron-oxo species.[17]

We also speculate that spin acceleration could contribute to the high reactivity of many complexes of "redox-active" ligands. Though the catalytic activity of complexes with redox-active ligands like pyridinediimines has often been attributed to the ligand acting as an "electron reservoir",[34] an alternative explanation is that the nearby metal and ligand orbitals in these species gives a series of densely spaced electronic states whose accessibility cuts through the barriers that might exist for the desired reactions on a single potential energy surface. We look forward to future computational analysis of catalytic reactions of redox-active ligands, which could substantiate or refute this hypothesis.

■ CATALYTIC ALKENE ISOMERIZATION THROUGH SPIN ACCELERATION

Computations on quartet (high-spin Co^{2+}, 3 unpaired electrons, $S = 3/2$) and doublet (low-spin Co^{2+}, 1 unpaired electron, $S = 1/2$) states using a truncated diketiminate ligand indicate that spin-forbidden BHE again goes through a key MECP (Figure 7).[32] The overall barrier for BHE in $L^{trunc}Co(Et)$ is only 13 kcal/mol, and the doublet excited state is at 7 kcal/mol. This TS is much easier to reach than the 19 kcal/mol barrier and 14 kcal/mol excited state for the Fe analogue. The lower barrier predicts that cobalt should undergo more rapid BHE than the iron system described above. This enabled us to use BHE for an important catalytic reaction: alkene isomerization.

Alkene isomerization is a well-established organometallic reaction with high atom economy and redox economy.[35] However, it is rarely used in practice due to poor regioselectivity and stereoselectivity. The isomerization of terminal alkenes to internal alkenes typically gives mixtures of internal alkenes rather than a single isomer. Some catalysts give specific isomerization to the 2-position, but a mixture of Z and E isomers is obtained.[36] Isomerization has been studied for decades, but control over regioselectivity and stereoselectivity is rare.[37] Recent reports have featured Ru and Pd catalysts that can selectively convert terminal alkenes to 2-alkenes.[38−40] However, selectivity for the less thermodynamically stable Z isomer is much more difficult.[41] Weaver recently described light-driven isomerization of allylamines from E to Z isomers using Ir photosensitizers.[42] Note that many of these systems use precious metals as essential components.

In this context, we were excited to learn that $L^{tBu,iPr}Co(1-hexyl)$ is an active catalyst for the isomerization of a number of terminal alkenes selectively to the Z-2 isomer (Figure 8).[43] The reaction gives more than 80% yield and greater than 5:1 Z:E selectivity for 1-alkenes, homoallylsilanes, ketals, TBS-protected alcohols, and allylbenzene with 5% loading of cobalt catalyst (selected examples in Table 1). This demonstrates not only the
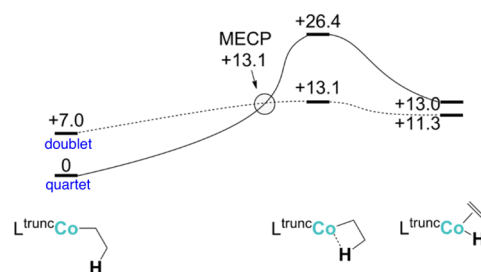

Figure 7. Potential-energy surfaces for BHE from cobalt−alkyl complexes analogous to those above in Figure 5. In this case of spin acceleration, the quartet flips a spin to go to the doublet surface during the transition state.
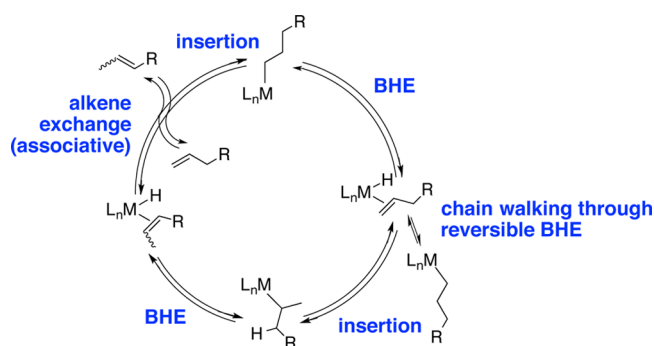
Figure 8. "Alkyl" mechanism for alkene isomerization,[1] emphasizing the β-hydride elimination (BHE) steps, chain walking, and alkene exchange.

Table 1. Selected Results for Catalytic Isomerization of Terminal Alkenes to Z-2-Alkenes[a]

Starting material	Product	Time (h)	Yield	E:Z	S.M. recov
		12	67%	1:7.2	3%
		40	89%	1:6.1	7%
		24	90%	1:6	3%
		12	87%	1:9.1	5%
		12	83%	1:5.6	5%

[a]5 mol% catalyst, 80 °C. Details in ref 43.

ability to substitute a base metal for platinum-group metals, but also that the inexpensive metal can give distinctive selectivity that improves the reaction. Analogous selectivity with a different cobalt complex was reported very recently by Hilt and uses a different mechanism than that described here.[44]

The catalytic isomerization reaction involves reversible BHE, which enables the cobalt to walk rapidly to the end of any alkyl chain (Figure 8). For example, addition of the 1-, 2-, or 3-substituted hexyl Grignard reagent to $L^{tBu,iPr}$CoCl gave $L^{tBu,iPr}$Co(1-hexyl), which is the most stable isomer for electronic reasons.[31] The chain walking process moves cobalt down the entire length of a linear chain, as shown by the catalytic isomerization of 1-^{13}C-1-hexene to equal amounts of the two isotopologues of 2-hexene and the two isotopologues of 1-hexene (Figure 9). Chain walking can be slowed by a substituent on the alkyl chain (see Figure 8, last row), because chain walking requires the formation of a tertiary Co-alkyl complex that is relatively high in energy.

Why is this reaction selective for the less thermodynamically favored Z isomer and for only 2-alkene? Our initial rationale was that the transition state for BHE (illustrated in Figure 7) requires the β-hydrogen to approach in the plane of the supporting diketiminate ligand.[43] When a secondary Co-alkyl complex is undergoing BHE to form an internal alkene, it must choose between two hydrogen atoms, and this choice
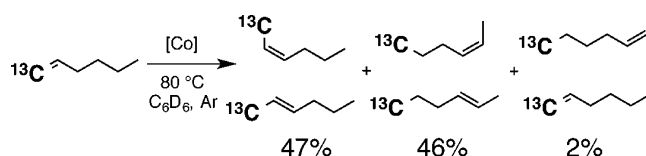

Figure 9. Carbon-13 labeling experiments show that the cobalt migrates down the entire chain, which requires the transient formation of 3-hexene complexes even though free 3-hexene is not formed. This finding indicates that the entire chain-walking process occurs without dissociation of alkene and suggests that the selectivity-determining step is alkene exchange.

determines the stereochemistry of the double bond in the product (Figure 10). We surmised that the choice between the hydrogen atoms could be influenced by the bulk of the supporting ligand above and below the plane, which favors putting the two alkyl substituents of the incipient alkene on the same side to give the Z isomer. If both of these alkyl substituents are larger than methyl (necessary to form the unobserved 3-hexene), then the transition state would suffer from a syn-pentane interaction between the substituents.

However, this explanation is not the full story because, as mentioned above, BHE must be able to transiently give 3-hexene cobalt complexes during the experimentally demonstrated process of walking all the way down an alkyl chain (Figure 8). Thus, the BHE-based model for selectivity does not adequately explain the selectivity for 2-hexene over 3-hexene as a product. Additionally, 3-hexenes enter the catalytic cycle very sluggishly, suggesting that free 3-hexene is not an intermediate in the reaction. Therefore, we conclude that 3-hexene complexes of cobalt are involved but do not release alkene. These results are best accommodated by a revised model in which alkene exchange is selectivity-determining and proceeds through an associative mechanism, and therefore, the selectivity of the products derives from the differential ability of alkenes to access a cobalt bis(alkene) complex. The cobalt(3-hexene)-(hydride) complex would have the most crowded cobalt environment and be the least likely to accommodate another alkene and release 3-hexene. 1-Hexene and Z-2-hexene are the easiest to release, but over time, the more stable Z-2-hexene accumulates at the expense of 1-hexene because of its greater thermodynamic stability. This new rationale needs to be supported by further experiments and computations. In addition, note that the alkene–hydride cobalt(II) complexes are predicted to have nearby quartet and doublet states,[32] and therefore, spin acceleration may influence the outcome of the alkene exchange step as well.
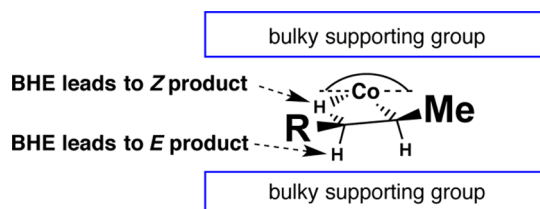

Figure 10. Steric model for the selectivity of alkene isomerization by $L^{tBu,iPr}$Co(alkyl) complexes.[43] This model treats BHE as the selectivity-determining step, but the results in Figure 9 suggest instead that alkene exchange may be selectivity-determining.

CONCLUSIONS AND FUTURE WORK

This research shows that spin acceleration can facilitate β-hydride elimination, one of the fundamental reactions of organometallic chemistry.[30a] The spin acceleration contrasts with other cases where spin-state changes hinder reactions.[45] Thus, a change of spin can accelerate or slow a reaction, depending on whether the MECP is along the reaction coordinate or not, as emphasized by Poli.[20] We hypothesize that the specific geometric requirements of the MECP can be used to bring about selectivity that is distinctive to the specific spin-state change. In the future, we anticipate that clever design of ligand bulk, in combination with analysis of the geometrical preferences of different spin states, will enable chemists to take full advantage of the special opportunities of base metal complexes with relatively weak ligand fields.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

Biography

Patrick Holland grew up in Ohio and Florida and was trained at Princeton University (A.B. 1993) and the University of California at Berkeley (Ph.D. 1997). After organometallic research at Berkeley with Richard Andersen and Robert Bergman, he pursued postdoctoral research on copper-O₂ and copper-thiolate chemistry with William Tolman at the University of Minnesota. Emboldened by his synthesis of the first synthetic three-coordinate copper(II) complexes with Tolman, his independent research at the University of Rochester initially focused on systematic development of the properties and reactions of three-coordinate complexes of iron and cobalt. Since then, his research group has broadened its studies to iron-N₂ chemistry, reactive metal—ligand multiple bonds, iron—sulfur clusters, engineered metalloproteins, redox-active ligands, solar H₂ production, and the mechanisms of organometallic transformations at base metal complexes. In 2013, he moved to Yale University, where he is now Professor of Chemistry. His research has been recognized with an NSF CAREER Award, a Sloan Research Award, a Fulbright Fellowship, a Blavatnik Award for Young Scientists, and election as a Fellow of the AAAS. He is also an avid musician with interests in classical and jazz music.

ACKNOWLEDGMENTS

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