Communication

Simple, Chemoselective, Catalytic Olefin Isomerization

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Simple, Chemoselective, Catalytic Olefin Isomerization

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Supporting Information Placeholder

ABSTRACT: Catalytic amounts of Co(Sal^{tBu,tBu})Cl and organosilane irreversibly isomerize terminal alkenes by one position. The same catalysts effect cycloisomerization of dienes and retrocycloisomerization of strained rings. Strong Lewis bases like amines and imidazoles, and labile functionality like epoxides are tolerated.

Metal-catalyzed alkene isomerization[1,2,3] is a powerful chemical transformation that achieves what classical techniques cannot–a [1,3]-hydrogen shift–but can be limited by the ability of carbophilic Lewis acids to coordinate weakly Lewis basic and weakly back-bonding alkenes.[4] Similarly, metal-catalyzed alkene *cyclo*-isomerization[5] can achieve the equivalent of a pericyclic ene reaction under generally mild conditions, but usually requires one or more alkyne, allene or butadiene functions due to the facile coordination of these species with transition metals, especially palladium.[6] Cycloisomerizations involving only nonconjugated alkenes are challenged by the weak Lewis-basicity of electron-neutral C-C double bonds.[7,8] Consequently, sterically encumbered alkenes are difficult to engage and strong Lewis bases like nitrogenous heterocycles or aliphatic amines are not well tolerated.[9,10] Here we report alkene isomerizations, polyene cycloisomerizations, and alkene retrocycloisomerizations that tolerate Lewis basic functionality, including amines, imidazoles and epoxides, all triggered by a Co(Sal^{tBu,tBu})Cl / silane catalyst system.[11] Experimental observations combined with literature precedent suggest a radical isomerization[12,13] via reversible hydrogen atom transfer (HAT).[14,15] Notably, the efficiency of the reaction appears to depend on the persistence of an intermediate carbon-centered radical, which is tied to the stability a metal-ligand 'counter-radical'. These observations are consistent with the effect of cobalt-ligand electronics on polydispersity and chain length in reversibly terminated radical polymerization.[15,16]

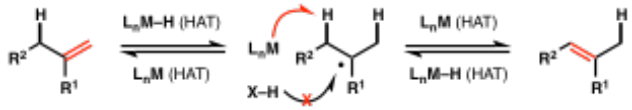
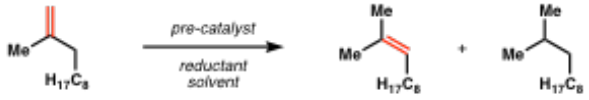


Figure 1. Can isomerization predominate over hydrogenation in a HAT equilibrium?

We recently reported manganese- and cobalt-catalyzed alkene hydrogenations that deliver thermodynamically-preferred stereoisomers via a radical mechanism.[17] We proposed that the first step of the reaction involves hydrogen atom transfer (HAT) from a metal hydride,[18,19] which may be operative in analogous Mukaiyama-type[20] radical hydrofunctionalization reactions.[21,22,23,24,25,26] Since mechanistic studies of known HAT-mediated reactions implicate reversible carbon-radical formation,[14a,b] it seemed reasonable that an appropriate ligand sphere on manganese or cobalt might promote an alkene isomerization along a radical reaction path and prevent reduction (Figure 1).[27]

A screen of metal catalysts, reductants and solvents that are known to effect Mukaiyama-type radical hydrofunctionalization was conducted in search of isomerization reactivity (**1→2**, Table 1). We found that cobalt salen complexes[28,29] in benzene with phenylsilane as a hydrogen source under anaerobic conditions afforded a high yield of isomer and little to no hydrogenation (entry 1, 8–10), whereas most other metal complexes known to participate in radical hydrofunctionalization gave either reduction or poor conversion (entries 2-6). Solvent does not play a major role, although benzene is superior. Phenylsilane proved to be the best reductant. Polymethylhydrosilane (PMHS) could also be used but Et_3SiH (TESH) failed (entries 10 and 11).

Table 1. Products from common Mukaiyama conditions.



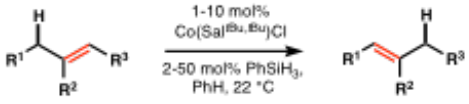
1 2 3

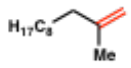
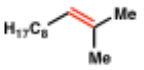
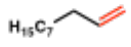
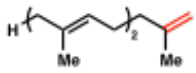
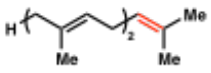
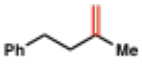
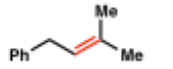
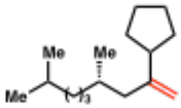
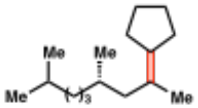
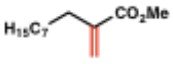
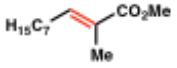
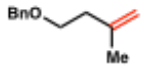
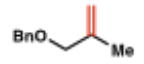
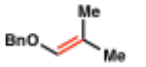
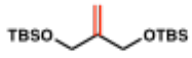
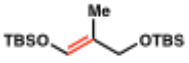
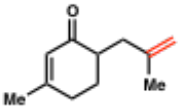
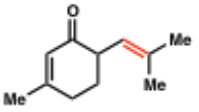
entry	conditions[a]	%1[b]	%2[b]	%3[b]
1	1 mol% Co(Sal^{tBu,tBu})Cl, 2 mol% $PhSiH_3$, PhH, 22 °C[c]	4	96	0
2	10 mol% $Mn(dpm)_3$, 2 equiv. $PhSiH_3$, *i*-PrOH, 22 °C[c]	39[d]	0	16
3	2 equiv. $Fe(oxalate)_3$, $NaBH_4$, MeCN/H_2O/*i*-PrOH, 0 °C[c]	34	1	1
4	50 mol% $Fe(acac)_3$, $PhSiH_3$, EtOH, 60 °C	28[d]	0	57
5	50 mol% $Fe(acac)_3$, $PhSiH_3$, PhH, 60 °C	65[d]	0	0
6	5 mol% $Co(acac)_3$, $PhSiH_3$, PhH, 60°C	99	0	0
7	5 mol% salcomine-Cl, $PhSiH_3$, PhH, 60°C	65	20	6
8	1 mol% Co(Sal^{tBu,tBu})Cl, $PhSiH_3$, Me_2CO, 22 °C[c]	5	94	<1
9	1 mol% Co(Sal^{tBu,tBu})Cl, $PhSiH_3$, CH_2Cl_2, 22 °C[c]	17[d]	63	2
10	5 mol% Co(Sal^{tBu,tBu})Cl, 2 equiv. PMHS, PhH, 22 °C[f]	4[d]	78	0
11	2 mol% Co(Sal^{tBu,tBu})Cl, 40 mol% TESH, PhH, 22 °C[f]	98	0	0
12	5 mol% Co(Sal^{tBu,tBu})Cl, 50 mol% AIBN, PhH, 80 °C[f]	86	11	0

[a]under Ar, 1 h unless noted; [b]according to GC-FID; [c]after 3 h; [d]multiple unidentified products were observed; [e]under air; [f]after 24 h

Since the metal complex abstracts a hydrogen atom from the reaction intermediate, silane can be used catalytically (2-10 mol%). In a similar way, AIBN functioned as a viable source of hydrogen atom at elevated temperature (entry 12), in support of a radical mechanism for reversible HAT and analogous to the mechanism associated with cobalt-porphyrin/ AIBN living radical polymerization.[30,31] Exclusion of either AIBN or the cobalt catalyst resulted in no isomerized product (see Supporting Information).

Table 2. Survey of terminal alkene isomerization.

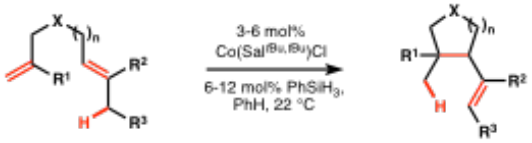


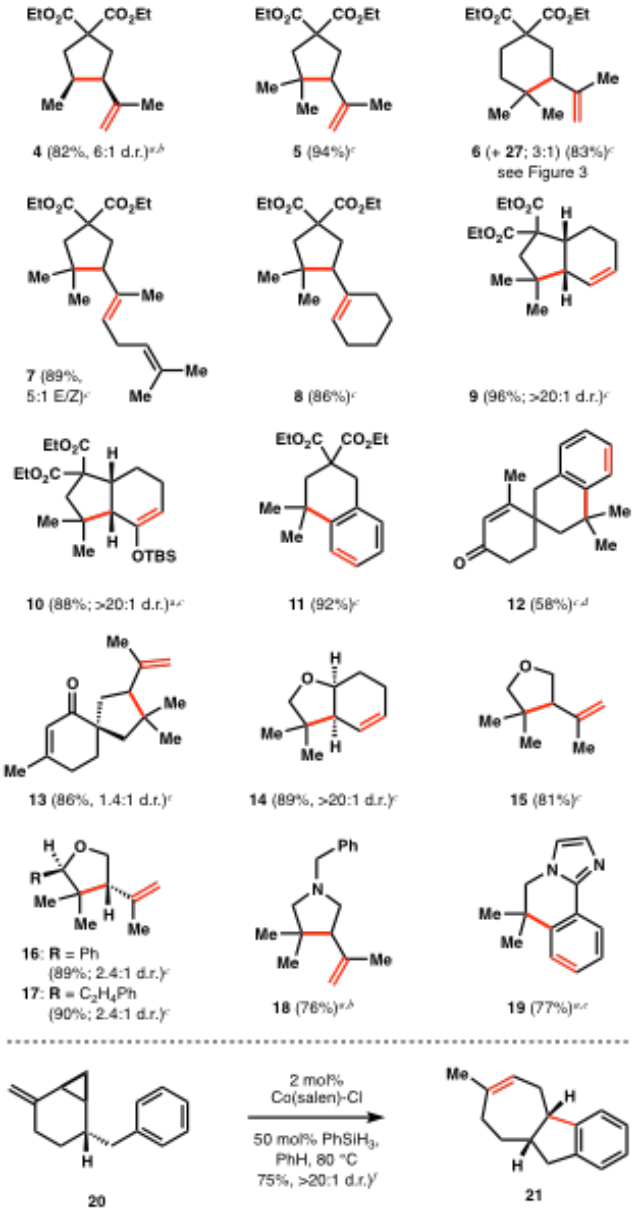
entry	substrate	product	yield	E / Z
1			91%[a]	–
2			83%[b,c]	3 : 1
3			65%[d]	–
4			83%[e]	–
5			90%[f]	–
6			69%[f]	10 : 1
7			77%[e]	–
8			81%[e]	–
9			92%[e]	3 : 1
10			74%[f]	–

[a]2 mol% [Co], 2 mol% [Si]; [b]10 mol% [Co], 50 mol% [Si] at 60 °C; [c]86:14 2-decene: decenes; [d]5 mol% [Co], 10 mol% [Si]; [e]3 mol% [Co], 6 mol% [Si]; [f]1 mol% [Co], 2 mol% [Si]

Due to ease of handling, Co(Sal$^{t\text{Bu},t\text{Bu}}$)Cl–a crystalline, air- and moisture-stable complex–formed the basis of an exploration of substrate scope (Table 2).[32] The choice of axial ligand (Cl, F, OAc) had only a minor influence on yield in a few cases. We quickly found that 1,1-disubstituted alkenes exhibited rapid reaction rates at room temperature (entry 1), whereas monosubstituted alkenes required elevated temperatures for high conversion (entry 2). The basis for the difference in temperature is discussed below. Other substitution patterns were less reactive, which allowed isomerizations to occur over a single position and then stop (six other minor decene isomers[33] totaled 14%: *avg*. 2% each). Thus, the isomerization appears not to be an equilibrium to the most stable alkene, but rather an irreversible reaction that discriminates against steric bulk, so that isomerization to a skipped diene (entry 3) proceeds without further isomerization to the conjugated diene, and isomerization to a homo-styrene is possible (entry 4). Nevertheless, isomerization of unsymmetrical alkenes (entry 5) selectively provides the tetrasubstituted alkene instead of the trisubstituted isomer, probably reflective of a

Table 3. Survey of diene cycloisomerization.





[a]at 60 °C; [b]5 mol% [Co], 10 mol% [Si]; [c]3 mol% [Co], 6 mol% [Si]; [d]at 100 °C; [e]6 mol% [Co], 12 mol% [Si]; [f]stereoisomer tentatively assigned by NOE

lower activation energy for methine C-H abstraction compared to the methylene C-H.[34] Electron deficient alkenes are cleanly isomerized to greater substitution (entry 6), which may be useful given the high prevalence but promiscuity of methylene lactone and ester motifs in complex, bioactive molecules. Homoallylic ethers may be isomerized to allyl ethers without further isomerization (entry 7), but given the proper substitution patterns, isomerization into conjugation with oxygen is possible (entry 8). Consequently, isomerization of a bis-allylic silylether can give rise to an aldol enolsilane (entry 9) and the mildness of the conditions prevents hydrolysis or elimination.

Similarly, allyl ketones can be isomerized into vinyl ketones with no conjugation (entry 10).

Given the established radical nature of intermediates in Mukaiyama hydrofunctionalization reactions and prior work in radical clock reactions,[35,21f,18b,24] we wondered if cyclization could outcompete hydrogen atom transfer to the metal, thus providing a mechanistically unique cycloisomerization of a polyene, and the equivalent of a pericyclic ene reaction. Indeed, these reactions work well to provide cycloisomerized products in good yield and diastereoselectivity. For instance, allyl prenyl and methallyl prenyl malonates cyclize cleanly to the disubstituted cyclopentanes **4** and **5**. Six-membered rings like **6** are also kinetically viable, although an inseparable linear isomer was produced as a minor product (this was optimized, see Figure 3. Polyenes (**7**) and rings (**8** and **9**) are competent acceptors, as are polarized alkenes like enolsilanes (**10**), enabling a mild Conia-ene like reaction that is difficult to achieve with Brønsted acid catalysis. Similarly, cycloisomerization is effective on aromatic rings, (**11** and **12**) unlike most metal-catalyzed processes, and under exceptionally mild conditions compared to Friedel-Crafts reactions. Diesters are not crucial, as **13** can be produced, albeit as a mixture of diastereomers. Thorpe-Ingold acceleration is also not necessary to achieive competitive cyclization versus isomerization, as tetrahydro furans **14**-**17** are produced cleanly. Remarkably, tertiary amines (**18**) and imidazoles (**19**) show no inhibition of catalysis. Also, reflecting the radical nature of the reaction, 4.1.0-bicycle **20** undergoes isomerization to **21** via cleavage of the cyclopropane[36] and addition to the pendant aromatic ring.

Analogous to this last example is the retrocycloisomerization of (–)-caryophyllene oxide (**22**, Figure 2), which is carried out under our standard conditions and provides a high yield of (–)-humulene oxide II (**23**). This showcase reaction enables the production of an expensive fragrance and flavor (**23**: $600 / 5 mg, Cheminstock) from a cheap commercial source (**22**: $0.28 / g, SigmaAldrich) and offers this HAT isomerization as a useful general method for modification of feed-stock chemicals to high-value materials. The strained terpene β-funebrene (**24**) can also be cleanly isomerized to α-funebrene (**25**) with no decomposition, in contrast to acidic conditions.[37]

The efficiency of cycloisomerization under these conditions is related to the persistence of the intermediate C-centered radical as measured by unimolecular cyclization, i.e. a radical clock competition against HAT to the metal-ligand complex. Since the cycloisomerization of **6** under standard conditions provided *ca*. 21% of the uncyclized isomer (Table 3 and Figure 3 below), we used this substrate to probe the effects of ligand electronics on radical persistence. An electron-deficient ligand (complex **A**) shows poor conversion, but more importantly it effects a low ratio of cycloisomerization to linear isomerization. Electron- neutral ligands (**B**, **C**) show moderate selectivity for cyclization, and an electron-rich ligand (**D**) amplifies cyclization. The diprenyl malonate **27** does not react under standard conditions using catalyst **C** or **D**. These effects of ligand electronics are consistent with equivalent changes in reversible hydrogen atom transfer and metal- carbon radical collapse in polymerizations mediated by cobalt salen complexes.[15c] That is, electron deficient complexes terminate the carbon-radical, whereas electron-rich complexes allow its persistence. Salcomine-Cl (**E**) is highly selective for cyclization, although we found it to be a poor catalyst for linear isomerization (Table 1, entry 7), consistent with radical capture (see Figure 4). The *tert*-Bu groups of catalyst **F** increase conversion but decrease cyclization.

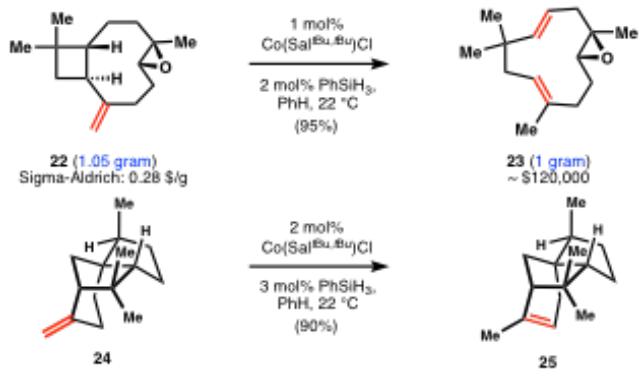
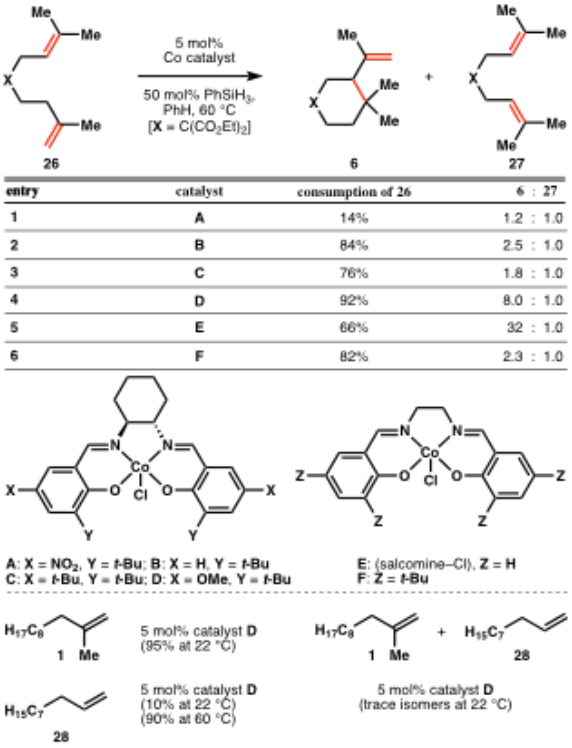


Figure 2. Modification of complex molecules.

In essence, our work is a unimolecular variant of catalytic chain transfer and living radical polymerization reactions,[16] as well as a link to the large and growing collection of Mukaiyama hydrofunctionalizations.[21] Catalytic chain transfer polymerizations using cobalt-salen catalysts implicate the intermediacy of a reactive, transient and unobservable metal-hydride as a product of reversible termination,[15,38] and Nojima observed metal-hydrides in Mukaiyama-type reactions.[35] It remains unclear in each individual report whether hydrofunctionalization proceeds via initial hydrometallation or hydrogen atom transfer (HAT),[39] but the low turnover number associated with the isomerization of **28** with **D** at ambient temperature, and its inhibition of the isomerization of **1** (Figure 3), are consistent with carbon radical/ metal collapse as an off-cycle, parasitic pathway, i.e. the hydrometallation product does not lie within the catalytic cycle (see Figure 4). Elevated tempera ture provides the activation energy to promote C-Co bond homolysis[15c,38] and reengage the catalytic cycle. It is unknown



entry	catalyst	consumption of 26	6 : 27
1	A	14%	1.2 : 1.0
2	B	84%	2.5 : 1.0
3	C	76%	1.8 : 1.0
4	D	92%	8.0 : 1.0
5	E	66%	32 : 1.0
6	F	82%	2.3 : 1.0

Figure 3. Effects of electronics and temperature.

whether collapse occurs in the solvent cage[40] or not. HAT is further supported by the absence of a proximal, empty valence for hydrometallation or cyclometallation on the putative Co-salen hydride complex.[31] Furthermore, the isomerization appears to be under kinetic, not thermodynamic control, since isopentenyl-prenyl malonate **26** cycloisomerizes, whereas diprenylmalonate **27** does not, even though both species would give rise to the same radical intermediate subject to the same unimolecular cyclization rate. Furthermore, terminal alkenes isomerize one position over and further isomerization is slow, likely a result of sterics.[41] A tentative catalytic cycle based on these observations is shown in Figure 4.

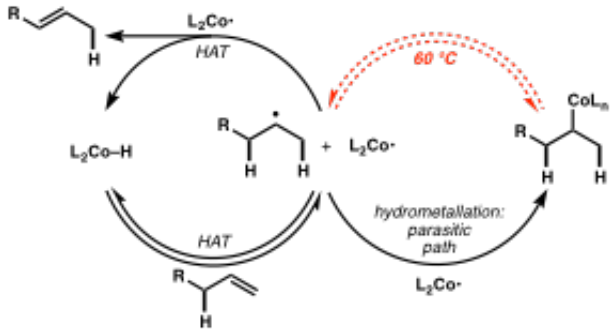


Figure 4. Hypothetical catalytic cycle.

In summary, we have shown that catalytic amounts of Co(salen$^{t\text{-Bu},t\text{-Bu}}$)Cl and organosilanes effect the isomerization of terminal alkenes, which takes the form of cycloisomerization if a pendant alkene is available, and retrocycloisomerization if the alkene is adjacent to a strained ring. These reactions likely proceed by reversible hydrogen atom transfer (HAT) to generate a transient carbon-centered radical. Given the tolerance of these reactions to functional groups, and the number of permutations available to salen ligand substitution, application and expansion of these tools are likely.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures and spectroscopic data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

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Author Contributions

‡These authors contributed equally.

Notes

A provisional patent (U.S. Serial No. 62/078,140) has been filed.

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Dedicated to Carlos F. Barbas, III in memoriam.

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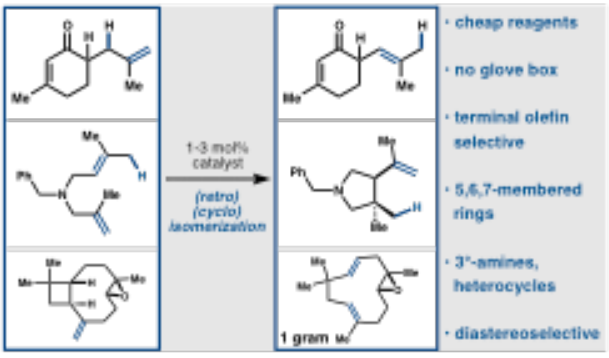

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