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From a Decomposition Product to an Efficient and Versatile Catalyst: The [Ru(η^5-indenyl)(PPh_3)$_2$Cl] Story

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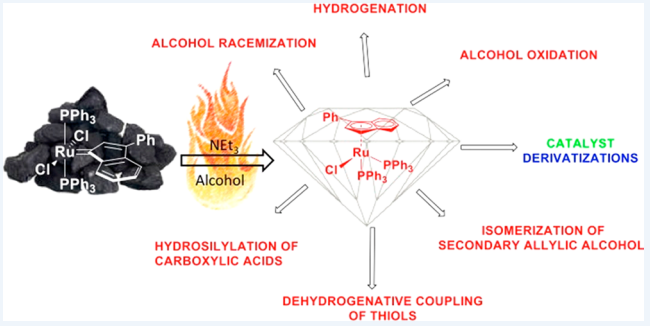
CONSPECTUS: One of the most important challenges in catalyst design is the synthesis of stable promoters without compromising their activity. For this reason, it is important to understand the factors leading to decomposition of such catalysts, especially if side-products negatively affect the activity and selectivity of the starting complex. In this context, the understanding of termination and decomposition processes in olefin metathesis is receiving significant attention from the scientific community. For example, the decomposition of ruthenium olefin metathesis precatalysts in alcohol solutions can occur during either the catalyst synthesis or the metathesis process, and such decomposition has been found to be common for Grubbs-type precatalysts. These decomposition products are usually hydridocarbonyl complexes, which are well-known to be active in several transformations such as hydrogenation, terminal alkene isomerization, and C−H activation chemistry. The reactivity of these *side products* can be unwanted, and it is therefore important to understand how to avoid them and maybe also important to keep an open mind and think of ways to use these in other catalytic reactions.



A showcase of these decomposition studies is reported in this Account. These reports analyze the stability of ruthenium phenylindenylidene complexes, highly active olefin metathesis precatalysts, in basic alcohol solutions. Several different decomposition processes can occur under these conditions depending on the starting complex and the alcohol used. These indenylidene-bearing metathesis complexes display a completely different behavior compared with that of other metathesis precatalysts and show an alternative competitive alcoholysis pathway, where rather than forming the expected hydrido carbonyl complexes, the indenylidene fragment is transformed into a η^1-indenyl, which then rearranges to its η^5-indenyl form. In particular, [RuCl(η^5-(3-phenylindenylidene)(PPh_3)$_2$] has been found to be extremely active in numerous transformations (*at least 20*) as well as compatible with a broad range of reaction conditions, rendering it a versatile catalytic tool. It should be stated that the η^5-phenyl indenyl ligand shows enhanced catalytic activity over related half-sandwich ruthenium complexes. The analogous half-sandwich (cyclopentadienyl and indenyl) ruthenium complexes show lower activity in transfer hydrogenation and allylic alcohol isomerization reactions. In addition, this catalyst allows access to new phenylindenyl ruthenium complexes, which can be achieved in a very straightforward manner and have been successfully used in catalysis. This Account provides an overview of how mechanistic insights into decomposition and stability of a well-known family of ruthenium metathesis precatalysts has resulted in a series of novel and versatile ruthenium complexes with unexpected reactivity.

The rationalization of possible deactivation pathways of a catalyst under various conditions is of great fundamental importance. It is necessary not only to test the mettle of any catalyst and learn how to avoid undesired side products or reduced reactivity but also to unlock new reactivity. Unraveling the identity of such species can, under the best-case scenario, provide novel reactivity opportunities. These new "catalysts" can exhibit completely distinctive reactivity compared with their "precursors". In such instances, the development of a facile and straightforward procedure for the synthesis of these new entities and a procedure to regenerate the original species can be a colossal task.

In olefin metathesis, the approach of uncovering the identity of the organometallic decomposition of the initial catalyst is becoming increasingly important. Several examples of decomposition analysis, side-product formation, and nonmetathesis reactions have been described.[1,2] Among such reaction pathways, the alcoholysis reaction of ruthenium precatalysts has generated significant interest. Initially revealed with first- and second-generation Grubbs' catalysts, the ruthenium metathesis active complexes decompose in the presence of primary alcohols to form the hydrido carbonyl complexes **1** and **2** (Scheme 1). The new hydrido catalysts have been shown to be highly active in alkene isomerization and hydrogenation reactions, as well as in multiple tandem processes.[3−5]

Extensively studied by Mol and Fogg,[6−8] and more recently examined *in silico* by Percy and Tuttle,[9] alcoholysis reactions have been demonstrated to occur via phosphine dissociation, and in the presence of primary alcohols, such as methanol, coordination of the oxygen to the ruthenium center. Through elimination of HCl (quenched by the base present), the methoxy compound **3**

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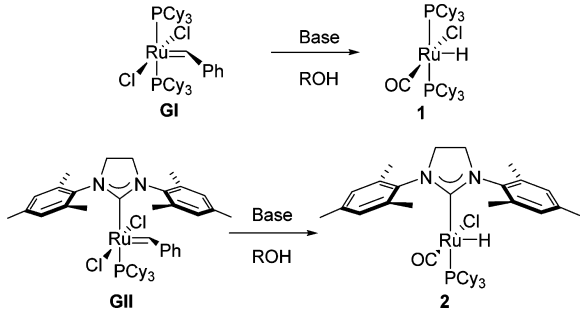
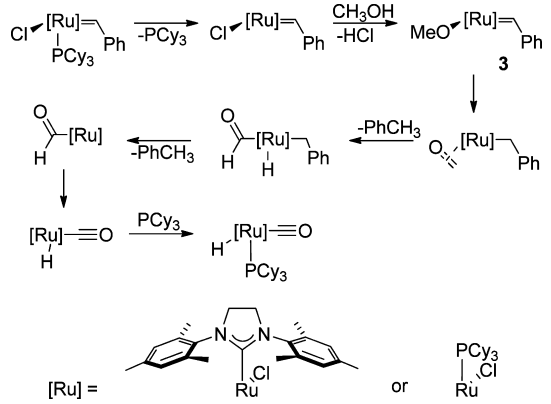
Scheme 1. Alcoholysis of First- And Second-Generation Grubbs' Catalysts



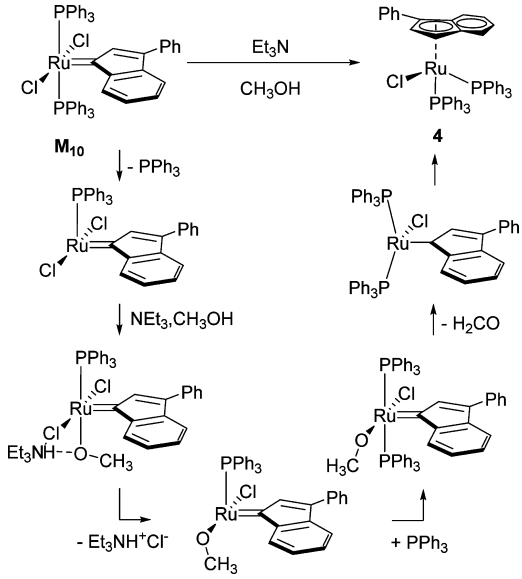
Scheme 2. Proposed Alcoholysis Mechanism of GI and GII



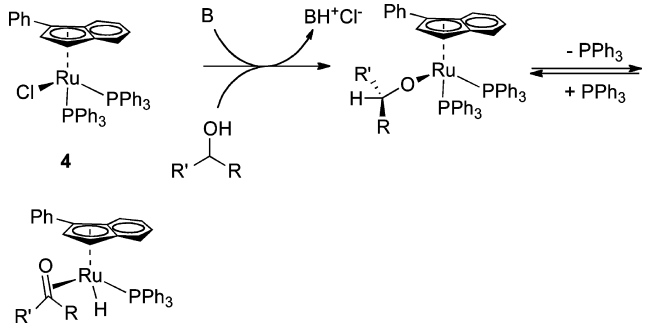
is formed, which immediately reacts with the alkylidene moiety via hydride transfer to generate, after additional hydride transfer from the benzyl moiety, toluene and a ruthenium species. This ruthenium complex undergoes a third hydride transfer and leads, after recoordination of the dissociated PCy_3 ligand, to the formation of the reported hydrido carbonyl complex (Scheme 2).[6,9]

A different behavior has been observed for the indenylidene-bearing metathesis complexes (Scheme 3). These complexes have revealed an alternative competitive alcoholysis pathway, where rather than forming the expected hydrido carbonyl complex, the indenylidene is transformed into a η^1-indenyl, which then rearranges to its more thermodynamically stable η^5-indenyl form. Our group first observed this behavior with $[RuCl_2(PPh_3)_2(3\text{-phenylindenylidene})]$ ($\mathbf{M_{10}}$), a valuable synthon for second and third generation indenylidene precatalysts.[10,11] Under basic conditions and in the presence of an alcohol, $\mathbf{M_{10}}$ rapidly decomposes into **4**. This rearrangement is

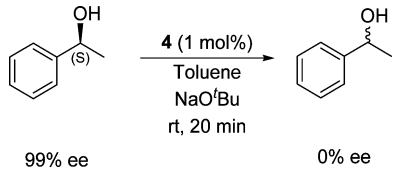
Scheme 4. Alcoholysis Mechanism Involving M_{10}



Scheme 5. α-Hydrogen Elimination and Insertion of Alkoxides into 4



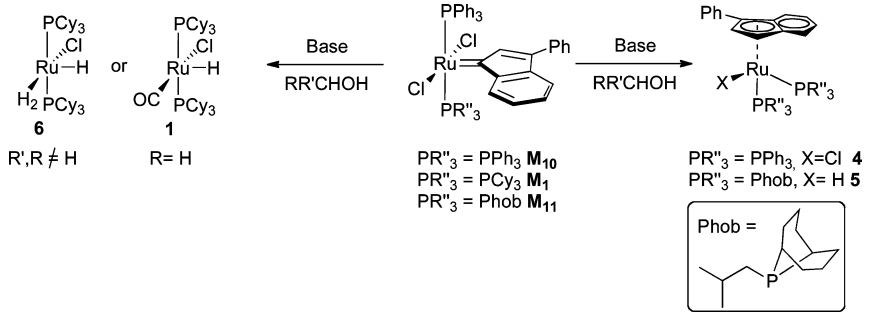
Scheme 6. Racemization of (*S*)-Phenylethanol



dependent on both the alkylidene moiety and the phosphine ligand involved (Scheme 3).[12−14]

The rearrangement is observed with $\mathbf{M_{10}}$ and with primary and secondary alcohols (Scheme 3). $[RuCl_2(PCy_3)_2(3\text{-phenyl-}$

Scheme 3. Alcoholysis of First Generation Ruthenium Indenylidene Precatalysts



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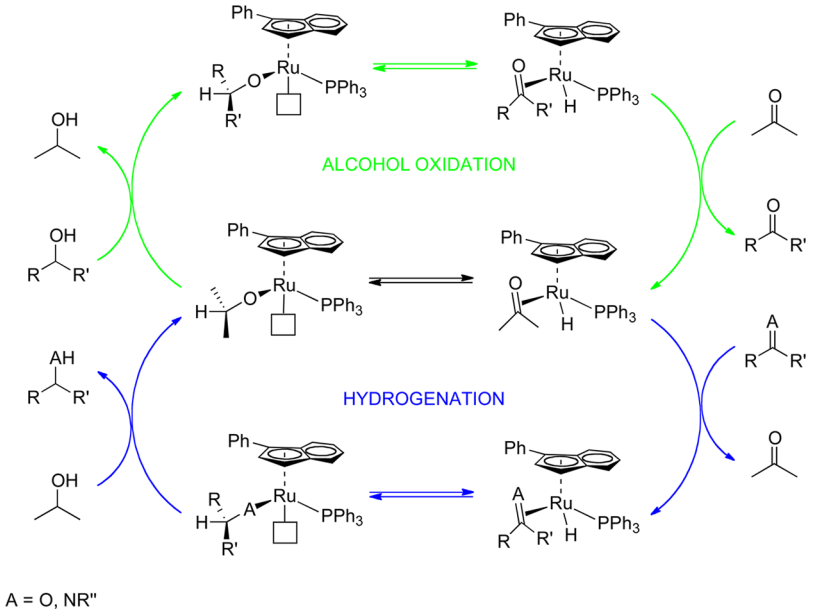
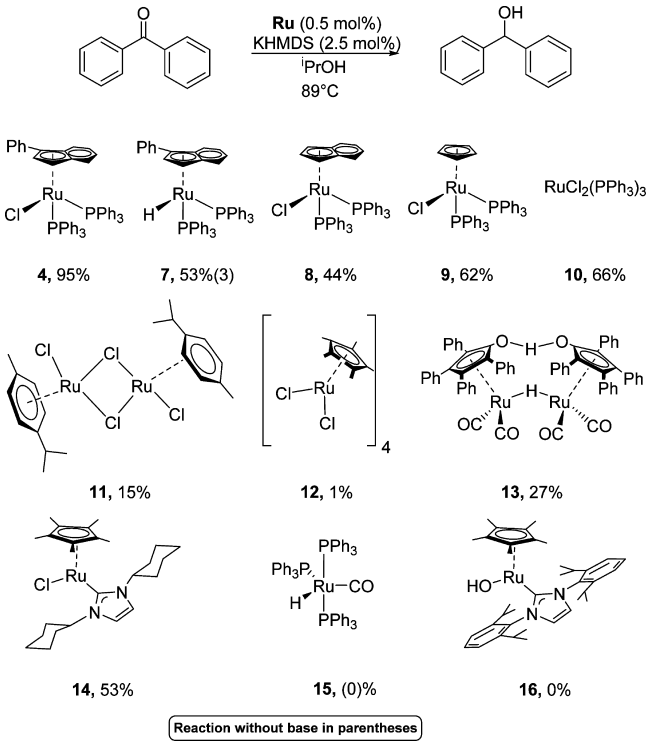
Scheme 7. Hydrogenation and Oxidation Processes via Use of Sacrificial Donor/Acceptor



Scheme 8. Transfer Hydrogenation of Benzophenone with Several Ruthenium Complexes



indenylidene)] ($\mathbf{M_1}$) exhibits a completely different behavior. In this instance, the indenyl rearrangement is inhibited, likely due to steric effects and the reduced flexibility of the phosphine ligand, yielding the analogous decomposition product obtained from **GI**. Surprisingly, [$RuCl_2$(^{i}Bu-Phoban)$_2$(3-phenylindenylidene)] ($\mathbf{M_{11}}$) decomposes via the indenyl rearrangement, also yielding a η^5-complex, but in contrast to **4**, the product further reacts and finally produces a mixture of hydride rotamers of [Ru(H)(η^5-3-phenylindenylidene)(^{i}Bu-Phoban)$_2$] (**5**) (Scheme 3).[13] Even though the ^{i}Bu-Phoban ligand has similar electronic and steric properties as PCy_3, the unique reactivity of the complex is probably due to increased flexibility generated by the free rotation of the isobutyl moiety, reducing steric hindrance sufficiently to achieve the η^5 complex. In the presence of secondary alcohols, $\mathbf{M_1}$ decomposes to the corresponding dihydrogen hydride **6**. This surprising behavior has also been observed for **GI** and its methylidene derivatives, confirming the generality of the process.[14] Second-generation metathesis precatalysts display the same behavior as the earlier generation under alcoholysis reaction conditions, but the possibility of N-heterocyclic carbene dissociation makes the system complex and more difficult to analyze.[14]

The unusual indenylidene to indenyl rearrangement occurs via dissociation of one phosphine and coordination of one molecule of alcohol to the metal followed by the release of one equivalent of HCl, which is promoted by the presence of triethylamine. After recoordination of the phosphine, one hydride is presumably transferred from the alkoxide to the indenylidene moiety via an agostic hydrogen transfer, releasing one molecule of the corresponding aldehyde and forming the η^1-indenyl species, which quickly rearranges to the final complex **4** (Scheme 4).[12,14]

The phenylindenyl complex **4** displays a similar structure as its arene ruthenium congeners that have been widely reported as either catalysts or synthons. However, the presence of a single phenyl group in the indenyl ring leads to the unique reactivity observed for **4**.[15−18]

What has emerged from the initial decomposition of an olefin metathesis study is an understanding of how a major decomposition product forms and how *maybe* this decomposition process can be exploited and novel chemistry can be developed. Some may call it an example of "making lemonade from lemons". Some of us, of a more optimistic nature saw that maybe novel vistas in reactivity could be explored using this decomposition product.

Our line of thinking then turned to potential catalytic uses and our first thoughts were about the involvement of alcohols in the synthesis of the complex and its possible involvement in reactions involving alcohols. Early experiments revealed that **4**

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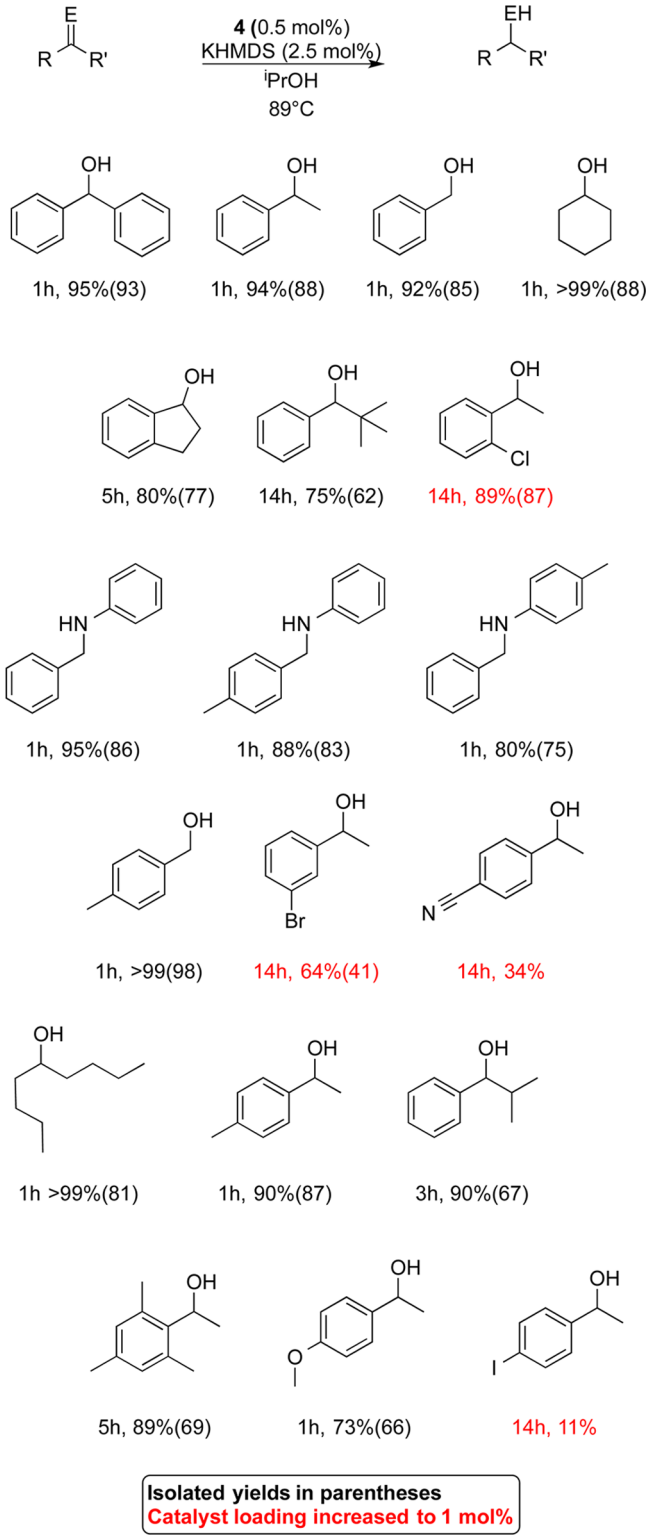
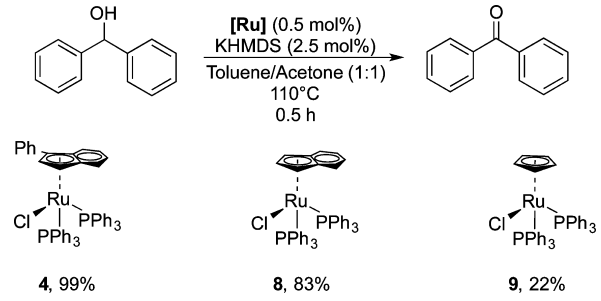
Scheme 9. Hydrogenation of Ketones, Aldehydes and Imines via a Transfer Hydrogenation Mechanism



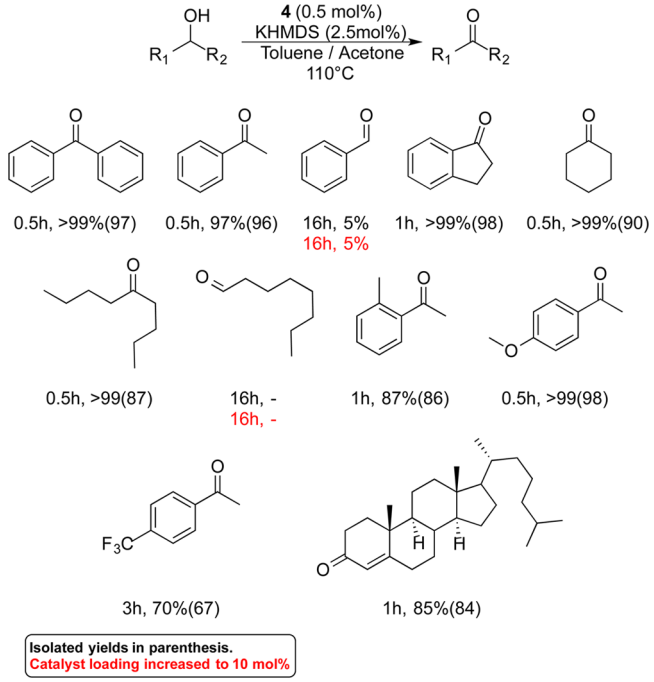
appeared to facilitate transfer hydrogen via α-hydrogen elimination and insertion of alkoxides (Scheme 5).

To further capitalize on this initial observation we reasoned that a potential important application would be the racemization of chiral secondary alcohols. Racemization protocols are especially interesting because they are often involved in industrial syntheses to obtain enantiomerically pure compounds, allowing,

Scheme 10. A Comparison of Reactivity between Alcohol Oxidation Catalysts



Scheme 11. Oxidation of Secondary Alcohols via Oppenauer Oxidation Mechanism



in combination with the appropriate enzyme, the possibility to resolve a racemic mixture of alcohols into an enantiomerically pure compound in a dynamic kinetic resolution (DKR) process.[19−22] Using (*S*)-phenylethanol as a model substrate, the reaction was performed in toluene at room temperature in the presence of sodium *tert*-butoxide to generate the active catalyst. Within 20 min, complete racemization was achieved using 1 mol % of **4**. This outcome is comparable to the indenyl analogue used by Park et al.[23,24] To evaluate the limits of the catalyst activity for **4**, a catalyst loading as low as 10 ppm was shown to afford near-complete racemization (95%) in 14 h at room temperature, which gives an impressive turnover number (TON) of 7×10^8 and turnover frequency (TOF) of 5×10^7 h^{-1} (Scheme 6).[12]

We next reasoned that racemization processes can be thought of as consecutive alcohol oxidation and hydrogenation of the resulting carbonyl compound. Therefore, by adding a sacrificial substrate, it might be possible to separate the two processes and evaluate the activity of **4** in the two different transformations: hydrogenation of carbonyl moieties by addition of isopropanol (hydrogen source) and alcohol oxidation by addition of a ketone (sacrificial hydrogen acceptor) such as acetone (Scheme 7).[25−30]

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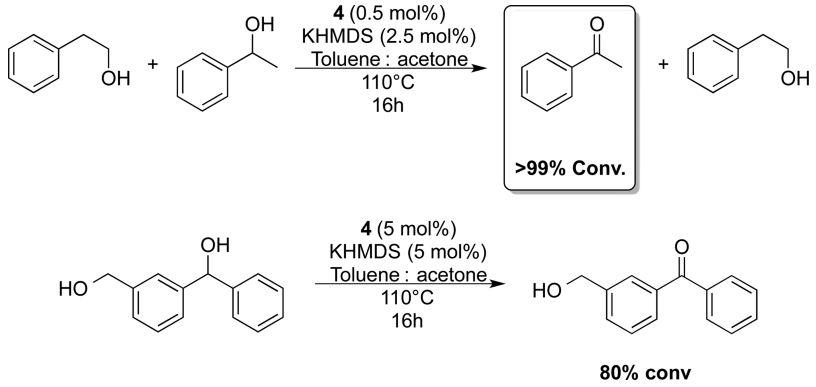
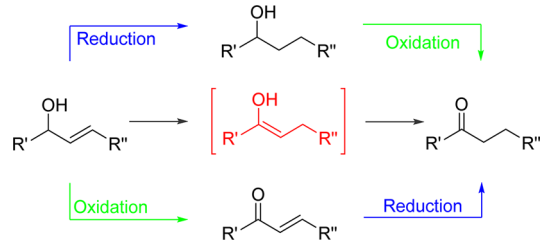
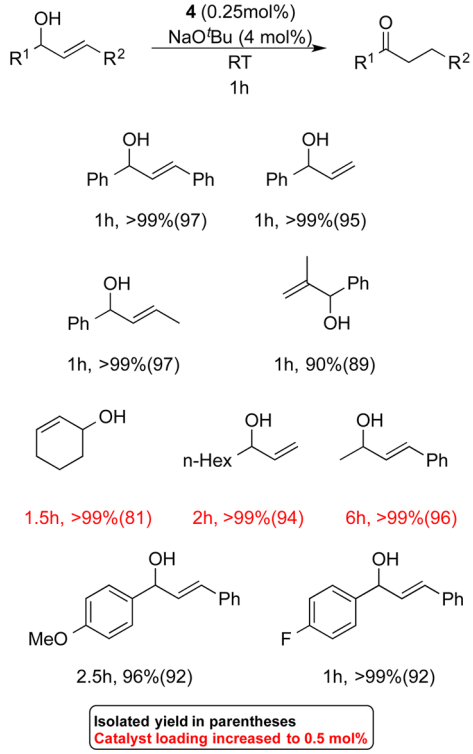
Scheme 12. Chemoselective Oxidation of Secondary Alcohols



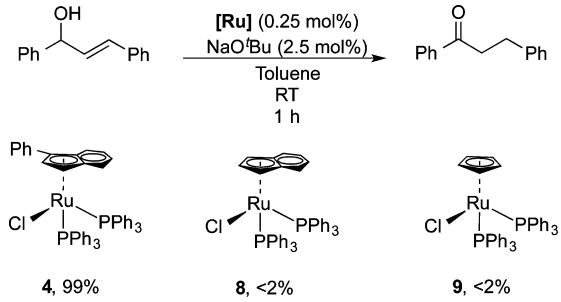
Scheme 13. Synthetic Approaches to Access Ketones from Allylic Alcohols



Scheme 14. Isomerisation of Secondary Allylic Alcohols



Scheme 15. Ligand Effect in Isomerisation of Allylic Alcohols



First, complex **4** displays remarkable activity in the hydrogenation of carbonyls via transfer hydrogenation compared with several commercially available arene analogues under the reaction conditions (Scheme 8). In particular, the introduction of the phenyl group at the 3-position of the indenyl moiety greatly increases the reactivity, possibly due to an electronic effect.[31] We must admit that the exact effect of the 3-Ph group is at this point pure speculation.

Complex **4** shows high activity for this transformation, reaching a maximum TON of 1920 using benzophenone as substrate. The system shows good compatibility with various functional groups, allowing the hydrogenation of either aromatic or aliphatic ketones, aldehydes, and aldimines. However, the complex shows lower reactivity with sterically hindered and electron poor ketones, requiring higher catalyst loadings to achieve reasonable conversions (Scheme 9).[31]

Additionally, the reasonable synthetic cost of **4** and its C_1 symmetry, could allow, with the addition of the proper chiral ligand, access to this transformation in a enantioselective manner. This has previously been shown for complex **11** in combination with the (*S*,*S*)-TsDPEN ligand by Noyori et al.[25]

The reverse process, namely, the oxidation of alcohols to the corresponding carbonyl compound, is affected in a different manner by **4**. Despite the existence of several *hydrogen scavenger free* oxidation procedures,[32−35] or others using more reactive reagents such as peroxides or oxygen,[36−41] there is a veritable demand for a simple and industrially useful process. Complex **4** was evaluated in the Oppenauer oxidation, where the substrate is easily oxidized via the transfer of two hydrogen atoms by the metal complex to a sacrificial ketone (Scheme 7).[28,30,42,43]

Complex **4** was found to be catalytically active for alcohol oxidation at room temperature using acetone as a hydrogen acceptor. However, in order to achieve the desired product efficiently in shorter times, the reaction was found to operate optimally at 110 °C using toluene as a cosolvent. Under these conditions benzophenone is oxidized in only 0.5 h with 0.5 mol % of catalyst. Remarkably, complex **4** surpasses the reactivity of its analogues, namely, complex **8** and **9** (Scheme 10) in the Oppenauer oxidation, achieving a maximum TON of 1250 and a relatively high TOF of 400 h^{-1}. These results demonstrate the

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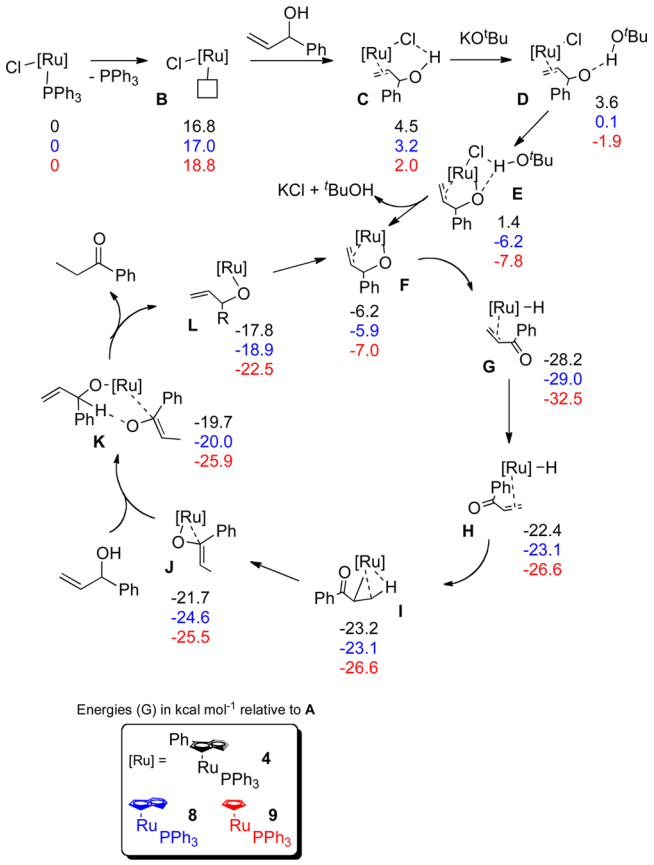
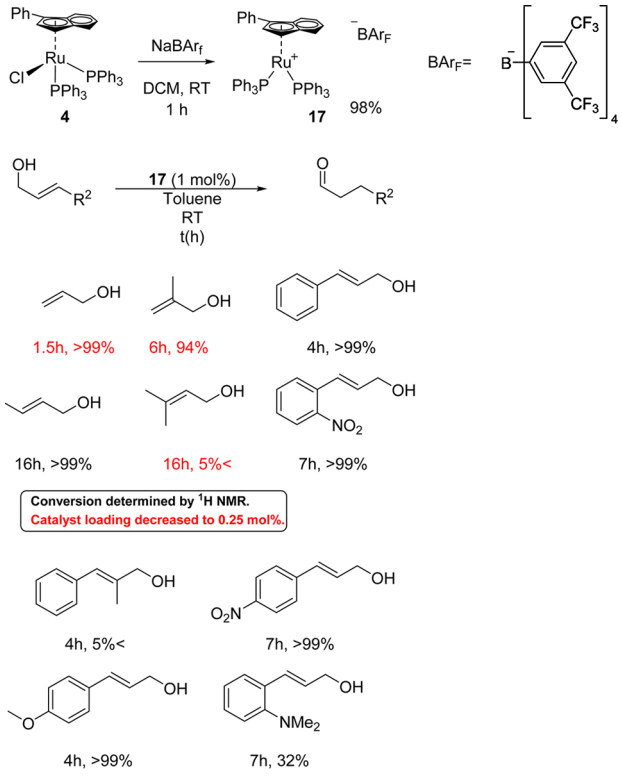
Scheme 16. Proposed Mechanism with Potential Energy Surfaces (PES) of the Isomerization of the Allylic Alcohols with the Ruthenium Arenes 4, 8, and 9[a]

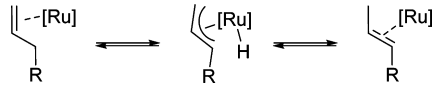


[a]Energies in kcal/mol. Level of theory M06L/TZVP//BP86/SVP. Thermochemical terms calculated at p = 1254 atm.

Scheme 17. Isomerization of Primary Allylic Alcohols with 17



Scheme 18. Isomerization of Terminal Olefin



beneficial effect, of using phenylindenyl as a ligand in this transformation (Scheme 10).[44]

The system displays high compatibility toward several bases and "green" solvents. In particular, it is possible to carry out the alcohol oxidation using isobutyl methyl ketone, which is considered a greener hydrogen acceptor than acetone.[44]

The process presents remarkable activity toward secondary alcohols, achieving full conversion of the desired aliphatic and aromatic ketones in 1 h. Alcohols bearing electron-withdrawing substituents are less prone to oxidation than their electron-rich analogues. Sterically hindered aromatic compounds are slightly more difficult to oxidize; showing similar behavior as in the reduction of carbonyls (Scheme 11).[44]

Surprisingly, complex **4** shows no activity in the oxidation of primary alcohols to aldehydes (Scheme 11). This high chemoselectivity was demonstrated in two competition experiments, in which only the secondary (vs primary) alcohol was oxidized in both cases (Scheme 12).[44]

A related transformation, namely, the redox isomerization of allylic alcohols because it also involves the α-hydrogen elimination/insertion of alkoxides, was next examined and appeared a good test of the catalytic activity of **4**. This methodology represents a powerful, elegant, and green method to prepare carbonyl compounds, where otherwise a two-step sequence of oxidation and reduction would be required (Scheme 13).[45−50]

Despite the numerous existing metal-catalyzed processes for this reaction,[47,50,51] the operational conditions and substrate compatibility still present significant limitations in particular in the isomerization of primary allylic alcohols.

Complex **4** displays extremely high activity in this transformation, isomerizing secondary allylic alcohols at room temperature and tolerating a reasonable degree of substitution at the vinyl moiety (Scheme 14).[52]

Internal and terminal benzyl and aliphatic allylic alcohols are isomerized with 0.25 mol % of **4** in 1 h. As for the transformations discussed previously, the electronic nature of the substrate greatly affects the observed reactivity. Aryl allylic alcohols bearing electron-donating substituents on the phenyl group are more difficult to isomerize. When the allylic alcohols are aliphatic or the phenyl substituent is on the olefin moiety, a higher catalyst loading (0.5 mol %) is required to reach full conversion. Monosubstituted alkenes and 1,1- or 1,2-disubstituted alkenes isomerize readily. However, trisubstituted alkenes do not react under these conditions. This methodology is restricted to secondary allylic alcohols, because the corresponding primary alcohols cannot be isomerized using **4**.[52] The performance of the system was evaluated at lower catalyst loadings and higher temperatures in order to probe the limits of reactivity of **4**, achieving a turnover number (TON) of 10000 and a turnover frequency (TOF) of 36000 h^{-1}. Both these values are highly competitive with the state-of-the-art.[49,50] Substitution of the arene ligand plays a crucial role in this transformation; complex **4**

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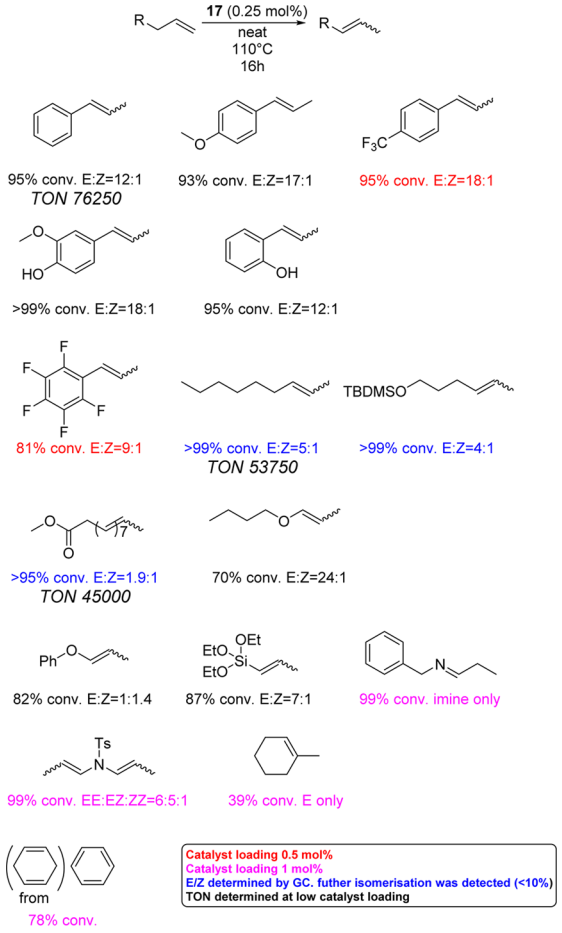
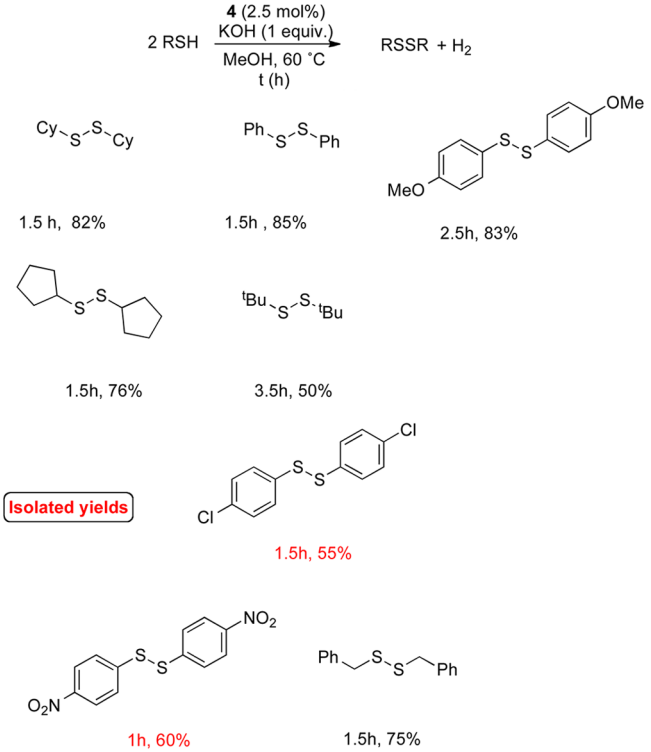
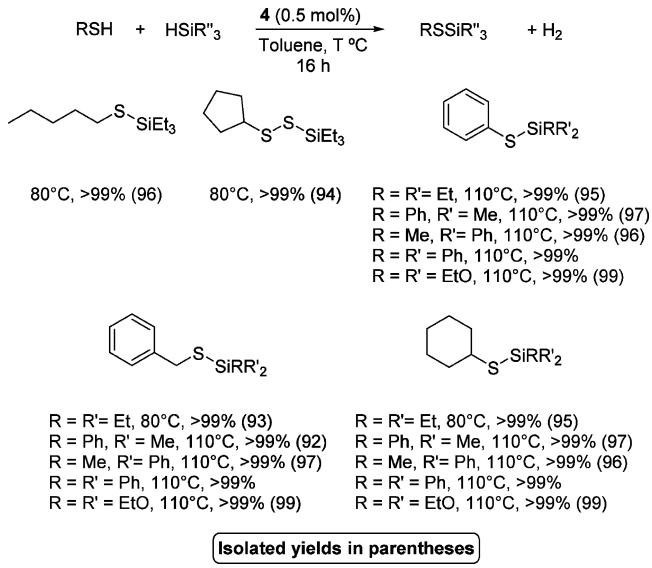
Scheme 19. Isomerization of Terminal Alkenes



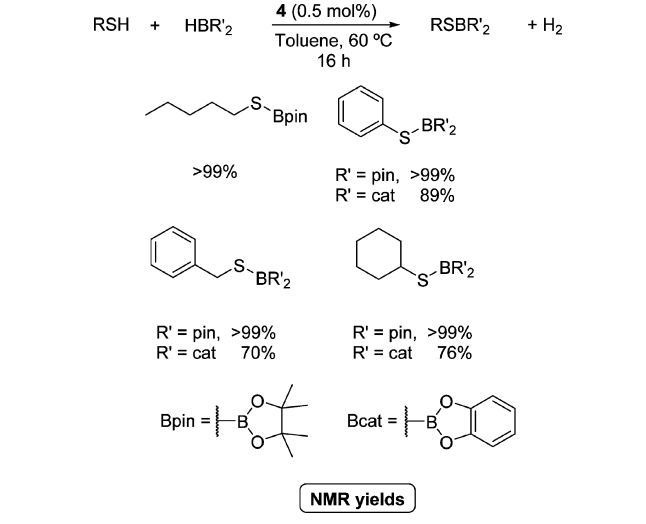
Scheme 20. Oxidation of Thiols to Disulfides



Scheme 21. Synthesis of Silylthioethers via Dehydrogenative Coupling



Scheme 22. Synthesis of Thioboronates via Dehydrogenative Coupling



shows high activity, while the congeners **8** and **9** are totally inactive under the same conditions (Scheme 15).[52]

Due to the marked differences in reactivity between **4** and its arene analogues (**8** and **9**), we, in collaboration with the Cavallo group, examined the reaction mechanism, comparing these results with those of **8** and **9**.[52] This was instigated because no quantification of the 3-Ph effect could be obtained other than by examining the relative catalytic performance of a series of related complexes.

First, using deuterium labeling experiments and support via DFT calculations, the isomerization was confirmed to proceed via a η^3-oxo-allyl mechanism (Scheme 16).[53,54]

The relative energetics of the isomerization reaction with the three catalysts showed that phosphine dissociation was favored for **4**, while the deprotonation and the chloride abstraction steps for this complex (**4**) exhibited the highest barriers.

In general, the calculations suggested that the intermediates along the reaction pathway catalyzed by the cyclopentadienyl analogue **9** are much lower in energy, although the overall

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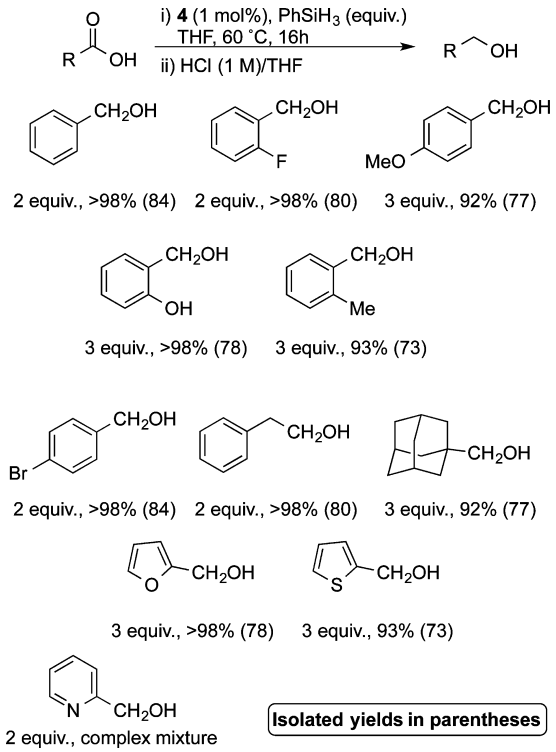
Scheme 23. Reduction of Carboxylic Acids via Hydrosilylation Mechanism



energetic spans (ΔE) are similar (31.5, 27.3, and 28.7 kcal mol^{-1} for **4**, **8**, and **9**, respectively). However, the barriers of each of the individual steps for **4** are typically smaller compared with those for **8** and **9**. This different reactivity may be explained by the lower decomposition rate of **4** (or intermediates derived from it) under the reaction conditions.

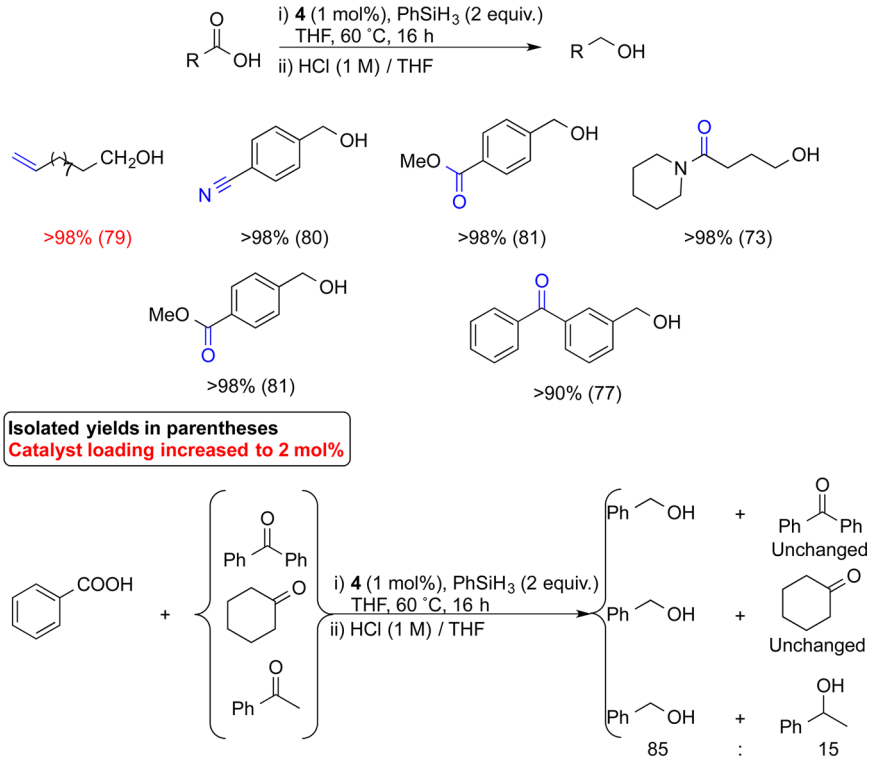
Notably, the energetics of the isomerization of primary and secondary allylic alcohols are rather similar, suggesting that the inability of **4** to isomerize primary allylic alcohols is not a consequence of thermodynamic or kinetic effects. In fact, the DFT calculations show that a faster isomerization for primary allylic alcohols would be expected, suggesting that the presence of base as catalyst initiator may be at the origin of a side reaction, presumably deprotonating the allylic alcohol coordinated to the ruthenium and leading to catalyst poisoning. In order to overcome this problem, we considered the use of a cationic complex derived from **4** for this transformation and thereby avoid the use of a base.[52]

The computational work directed our next synthetic target, namely, the isolation of a cationic analogue of **4**. This was achieved very simply by treatment of **4** with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate in dichloromethane for 1 h, leading to the formation of the cationic complex **17**, which, as it turns out and maybe now expectedly, efficiently isomerized primary allylic alcohols to the corresponding aldehydes at rt (Scheme 17).[52,55]

An additional process involving hydrogen transfer steps is the isomerization of terminal alkenes. In this case, instead of alkoxy coordination and the subsequent α-hydrogen elimination, the ruthenium complex coordinates to the olefinic bond and abstracts the allylic hydrogen, forming a η^3-allyl hydride intermediate. The hydride is then reinserted at the terminal position of the alkene moiety, in order to yield the thermodynamically more stable double bond and results in double bond isomerization (Scheme 18).[39]

This transformation is a very useful reaction, employed in industrial processes to equilibrate feedstocks or to achieve high-value molecules starting from easily accessible precursors.[56,57]

Scheme 24. Chemoselective Hydrosilyation of Carboxylic Acids



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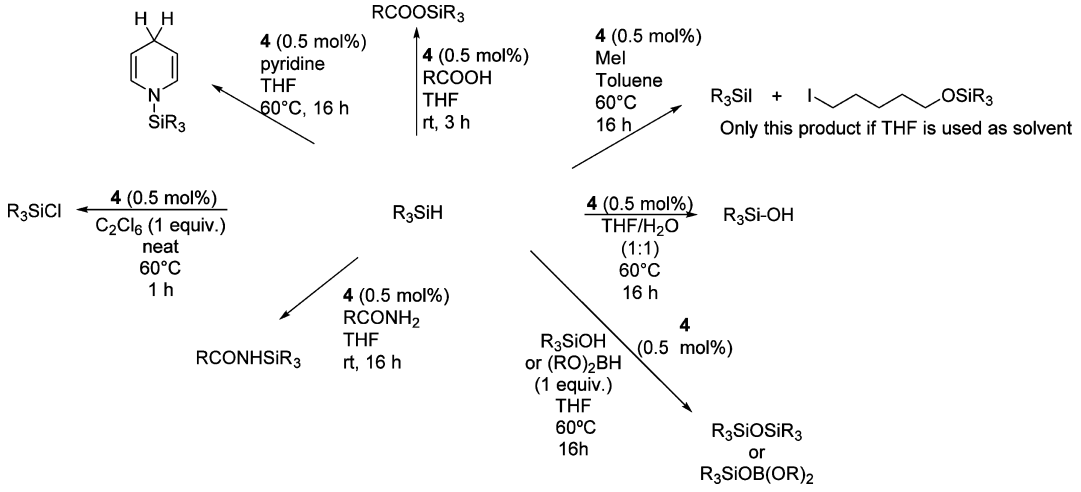
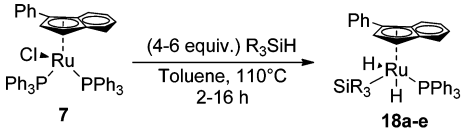
Scheme 25. Ruthenium-Catalyzed Transformations with Silanes[91]

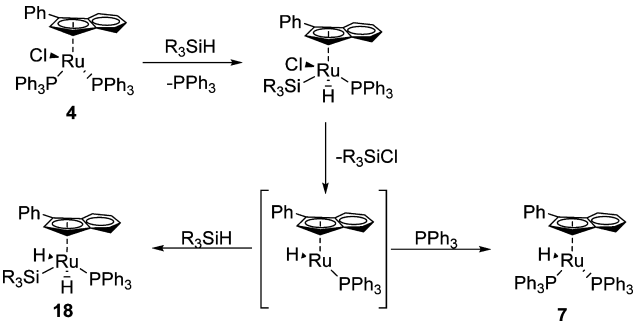


Scheme 26. Synthesis of $[RuH_2(SiR_3)(PPh_3)(3\text{-phenylindenyl})]$ (18a−e)

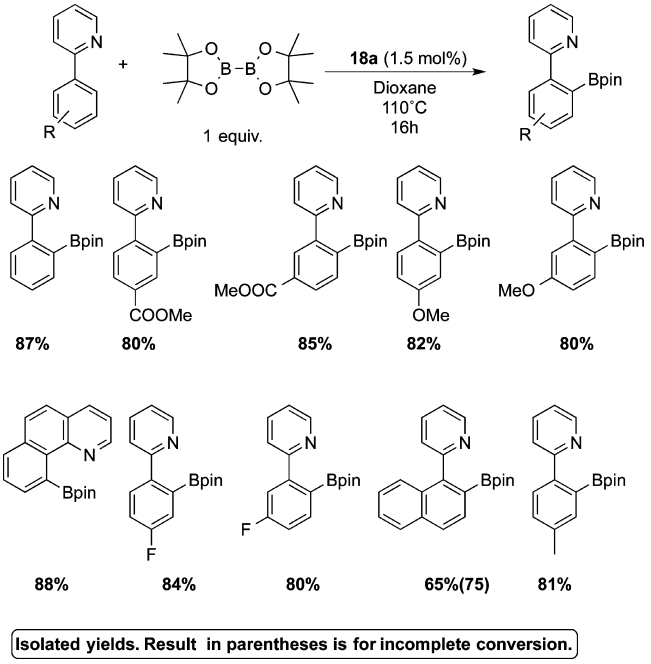


R_3Si = Et_3Si 85% yield **18a**
= EtO_3Si 69% yield **18b**
= $PhMe_2Si$ 60% yield **18c**
= Ph_2MeSi 65% yield **18d**
= Ph_3Si 70% yield **18e**

Scheme 27. Synthesis of $[RuH_2(SiR_3)(PPh_3)(3\text{-phenylindenyl})]$ (18a−e)



Scheme 28. Ruthenium Catalyzed Borylation of Phenylpyridine



Isolated yields. Result in parentheses is for incomplete conversion.

Moreover, in synthetic chemistry, this isomerization process permits easy preparation of vinyl from the corresponding allylic moieties, which are usually more easily prepared.[58] Several catalytic systems have been developed for this reaction;[59] however most of these are not particularly robust, especially in the presence of moisture or air. Under optimized conditions, high conversion to the internal alkene was achieved using only 300 ppm of **4** at 60 °C in THF (1:1 solvent/substrate) with 1-octene as the substrate. The introduction of **17** to this transformation broadens the scope of terminal olefin isomerization (Scheme 19). In addition, **17** was found to be air- and moisture-stable in the solid-state and reagent grade substrates can be used without need for their prepurification.[55]

The catalytic system is sensitive to steric bulk about the alkene moiety, displaying reduced reactivity and less effective stereoselectivity for more hindered substrates. Allyl ethers are more difficult to isomerize. Allylic amines, probably due to possible chelating effects with the metal, require a higher catalyst loading (1 mol %). The efficiency of **17** was evaluated with important industrial feedstocks, showing remarkable activity with 1-octene (petroleum-based feedstock), methyl-1-undecenoate (fatty ester feedstock), and allylbenzene (essential oil feedstock). Notably, the system is compatible with multistep procedures. For example, it is possible to combine the isomerization system with subsequent ethenolysis of the internal double bond in a telescoped isomerization−ethenolysis reaction, leading to the corresponding styrene compounds from their allylbenzene derivatives in high yield. These compounds are potentially valuable feedstocks for further functionalization.[55]

Because **4** is capable of oxidation catalysis, we reasoned that this catalyst could also effectively oxidize thiols to the corresponding disulfides by dehydrogenative dimerization. In fact, complex **4** is able to oxidize thiols to disulfides with remarkable activity. Aryl as well as primary and secondary alkyl thiols can be converted to the corresponding disulfides in good

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yields. Even sterically hindered tertiary alkyl thiols proved suitable substrates in the reaction, providing the corresponding disulfide in modest yields. Electronic factors were shown to play a role in the reactivity. For example, the presence of an electron-withdrawing group on the aromatic ring led to shorter reaction times but a slight erosion in yield (Scheme 20).[60]

Extending this process to other coupling partners, complex **4** also has the ability to couple thiols with silanes and boronates, generating the corresponding thioethers. Despite the great importance of these compounds in organic chemistry,[61] the number of reported methods for their preparation is limited.[62−64] Thiosilanes are usually obtained through the stoichiometric reaction of a chlorosilane and a metal thiolate. Only a few catalytic systems have been developed for this purpose.[65,66] Several thiols and silanes are well tolerated by the dehydrogenative coupling system, achieving high conversion in all cases. In fact, this transformation gave the best TON reported to date (TON = 200) (Scheme 21).[60]

This procedure can also be extended to access sulfur−boronate derivatives. These compounds present potential utility, particularly as borylation reagents,[69,70] and the reported transformation using **4** is the first catalytic process developed for the coupling of thiols with pinacol and catechol borane (Scheme 22).[60]

Complex **4** shows high versatility in this transformation, enabling the use of alkyl, benzyl, and aryl thiols and accessing the coupling products in good yields and high turnover numbers (TON 200).[60]

Complex **4** showed good reactivity in the reduction of ketones and the oxidation of alcohols and thiols. Unfortunately, this complex is not able to hydrogenate more oxidized functionalities such as carboxylic acid or esters. We reasoned that an alternative source of hydrogen might enable such transformations. The use of silanes as hydrogen source is an interesting hydrogenation alternative process. Catalytic hydrosilylation of carbonyl compounds has become an important alternative reduction strategy,[71−86] in particular compared with the stochiometric procedure using hydride reducing reagent (highly hazardous, impractical for large scale process, and oftentimes displaying very low chemoselectivities)[38,87,88] or metal-catalyzed hydrogenations using hydrogen (they generally require high pressures).[89]

Several metal- and metal-free catalyzed hydrosilylations of esters or amides to the corresponding alcohols and amines have been reported.[76−83] However, only a limited number of catalytic systems have been described for the hydrosilylation of free carboxylic acids. Therefore, in order to find a complementary procedure to our recently described metal-free hydrosilylation of amides and esters,[80] and in view of the high reactivity of **4** with silanes (*vide supra*), the reduction of carboxylic acids via hydrosilylation was then attempted.

Complex **4** shows very high activity and chemoselectivity in the hydrosilylation of benzoic acids in the presence of a broad range of substituents in either *ortho* or *para* positions, using phenylsilane as the reducing reagent. In general, heteroaromatic carboxylic acids are well tolerated, with the exception of picolinic acid, where a complex mixture of products was obtained (Scheme 23).[90]

Surprisingly, the catalytic system shows unexpected chemoselectivity, catalyzing the reduction of carboxylic acids to the desired alcohols in the presence of several reducible functional groups, such as alkenes, nitriles, tertiary amides, esters, and even ketones, which are well-known to be much more reactive under hydrosilylation or reduction conditions (Scheme 24). The chemoselectivity was investigated in a series of competitive reactions. The reduction of benzoic acid was investigated in the presence of three ketones. The system was found to be highly chemoselective toward the reduction of the carboxylic acid moiety, and only acetophenone is slightly reduced under the conditions employed (Scheme 19).[90]

Complex **4** shows catalytic activity in several other silane incorporating transformations, including the synthesis of silanols, chlorosilanes, silylesters, silylethers, and silylamides using a monosilane. It is also able to semihydrogenate pyridine.[91] This catalytic behavior is very similar to the hydrosilylation of pyridine using $[Cp^*Ru(PiPr_3)(NCMe)_2]PF_6$ reported by Nikonov et al. (Scheme 25).[92,93]

In order to gain insight into the active species and the possible intermediates involved in the above silane-mediated transformations, stoichiometric reactions with different silanes were carried out, resulting in the synthesis of a new library of ruthenium organosilane arene complexes **18** (Scheme 26).[94] This synthetic procedure shows high compatibility with various silanes and avoids the usual multistep synthesis reported in the literature for the preparation of analogous hydrido silyl ruthenium complexes.[92−101]

The mechanism proposed for the formation of **18a−e** proceeds via oxidative addition of the Si−H bond of the silane to ruthenium, associated with the displacement of a PPh_3 ligand, and is driven by the formation of the Si−Cl bond.[102] This transformation yields, as a side-product, complex **7**, probably due to the competitive and irreversible recoordination of PPh_3 to the $16e^-$ species. A large excess of silane is used to eliminate this *contamination* (Scheme 27).

A detailed characterization of these complexes revealed a possible hydride interchange mechanism and surely depends of the silicon moiety coordinated to the metal, probably via a δ-bond metathesis mechanism. Due to the peculiar properties of these complexes to easily interchange the oxidation state from Ru(II) to Ru(IV), we believed that these complexes would have interesting applications in C−H activation chemistry. Therefore, complexes **18** were evaluated in the C−H bond borylation of aromatic compounds, a reaction that has antecedents for rhodium and iridium[16,103] but is unprecedented for ruthenium.

The entire series of these ruthenium silane complexes were tested, and only **18a** proved catalytically active. The catalytic process using **18a** revealed this complex to be very active when pyridine is used as directing group, giving high yields of the borylated adducts by using the lowest catalyst loading reported to date for a ruthenium-mediated C−H activation reaction (Scheme 28).[104]

Complex **18a** shows remarkable activity with several phenylpyridine derivatives, and the electronic or the steric properties of the substrates do not affect the activity. Additionally, high regioselectivity is observed, leading to the 2-substituted product in all cases examined. The borylation procedure catalyzed by **18a** also exhibits interesting compatibility with other transformations, such as the Suzuki−Miyaura cross-coupling reaction.[94]

In summary, in this Account we have provided a description of our journey that began with attempting to understand the deactivation pathways of a series of olefin metathesis active ruthenium indenylidene complexes in alcohol solution. This led us into the unexpected adventure of exploring the reactivity of a *decomposition product*. Because the catalysis uncovered so far is quite wide ranging, we suggest that the *decomposition product* may potentially become more valuable than the starting alkylidene material. In fact, the recent commercial availability of [RuCl-

$(PPh_3)_2$(3-phenylindenyl)] (**4**)[105] (and the ease of synthesis of its derivatives) and the fact that these are active in *at least 20 different transformations* is truly remarkable and should lead, we hope, to its use in these and other transformations. In addition, it has been found that the presence of the phenyl moiety on the indenyl ring enhances not only the stability of the catalyst but also the reactivity in hydrogen transfer reactions and in dehydrogenative systems involving siliane compounds. In conclusion, the exploration of the reactivity of **4** allows us to state that it is much more than a *decomposition product* but represents a true *multitasking* catalyst.

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Notes

The authors declare no competing financial interest.

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Steven P. Nolan obtained his B.Sc. in Chemistry from the University of West Florida and his Ph.D. from the University of Miami where he worked under the supervision of Professor Carl D. Hoff. After a postdoctoral stay with Professor Tobin J. Marks at Northwestern University, he joined the Department of Chemistry of the University of New Orleans in 1990. In 2006, he moved to the Institute of Chemical Research of Catalonia (ICIQ) as a Group leader and ICREA Research Professor. In early 2009, he joined the School of Chemistry at the University of St Andrews, where he is a Professor and holds the Chair in Inorganic Chemistry and Catalysis.

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