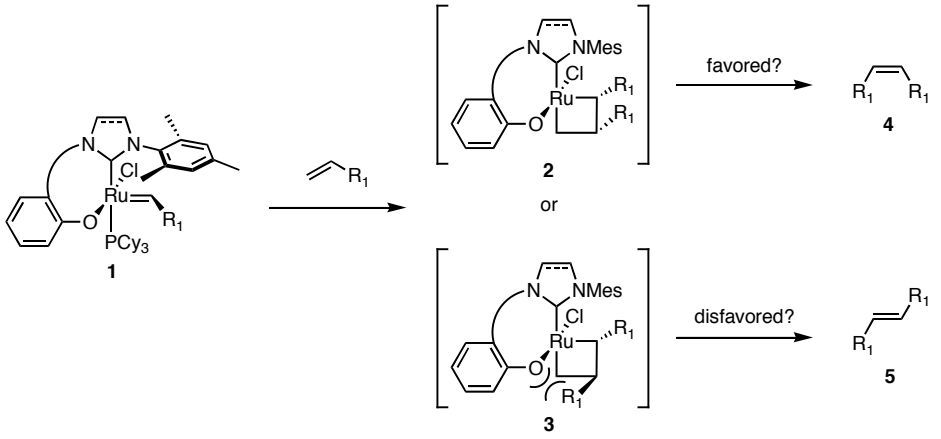
Appendix 2
Efforts toward a Ruthenium Olefin Metathesis Catalyst Bearing an *N*-Heterocyclic Carbene/Phenol Bidentate Ligand

Introduction

Two alkene isomers can be formed in an olefin metathesis reaction: the *E*-isomer or the *Z*-isomer. Rings that are five, six, or seven membered contain a *Z*-isomer, so there are no stereoselectivity issues in those ring-closing metathesis (RCM) reactions. On the other hand, macrocyclic RCM, cross-metathesis (CM), and ring-opening cross-metathesis (ROCM) can afford either isomer. All of the highly active ruthenium catalysts that have been developed to date favor the formation of *E*-olefins over *Z*-olefins in CM,[1] macrocyclic RCM,[2] and low-strain ROCM reactions,[3] most likely due to the thermodynamic nature of metathesis. In some cases, the *E*-isomer is not strongly preferred over the *Z*-isomer, but *E*/*Z* ratios do not typically drop below 1:1.[4] In general, CM reactions between monosubstituted, terminal olefins afford alkenes with *E*/*Z* ratios ranging from 2:1 to >20:1 depending upon the catalyst structure and the alkene sterics and electronics. There is almost no selectivity (1:1–2:1 *E*/*Z*) in ROCM reactions of strained rings.[5]

Because known ruthenium alkylidenes typically generate products enriched in *E*-olefins, catalysts that are selective for *Z*-olefins would be complimentary to the existing technology. In order to make a *Z*-olefin using metathesis, a ligand on the catalyst would have to interact with the metallacyclobutane and force both substituents on the ring to be syn to one another. At the time the work described below began, it was assumed that the incoming olefin bound trans to the *N*-heterocyclic carbene (NHC) ligand, and this has

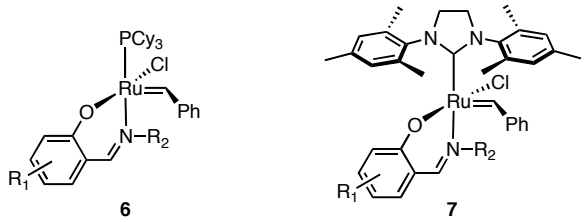
since been reinforced.[6] Based on this hypothesis, a bidentate NHC/phenol ligand structure was proposed (**1**) (Scheme A2.1). This type of ligand would desymmetrize the ruthenium center and could force the substituents on the metallacyclobutane to be syn (**2**).



Scheme A2.1. Proposed *Z*-selective catalyst structure and metallacycle intermediate.

There were a few examples of ruthenium catalysts bearing L,X-type bidentate ligands when this work began. Both classes of compounds had Schiff bases bound to ruthenium: one class had a phosphine ligand,[7] and the other had an NHC ligand[8] (Figure A2.1). None of the complexes in either series were highly active olefin metathesis catalysts; they formed 5-membered rings at elevated temperatures, and they were much less active in CM and macrocyclic RCM. A *Z*-selective catalyst would only be useful in a CM, macrocyclic RCM, or ROCM reaction, so these compounds were not adequate. The low activities of the Schiff base catalysts were attributed to the replacement of a chloride with a phenoxide and to the presence of a tethered dissociating ligand (the imine).[9] Although the phenoxide was an important part of the proposed ligands, it was thought that the catalyst activity would remain high due to the NHC and the monodentate, dissociating phosphine. Additionally, a small loss in reactivity due to the phenoxide may be advantageous; if the catalyst initially forms a *Z*-olefin from two

monosubstituted terminal alkenes and does not react with the 1,2-disubstituted alkene product (no secondary metathesis), there will be no erosion of the *Z*/*E* ratio over time.

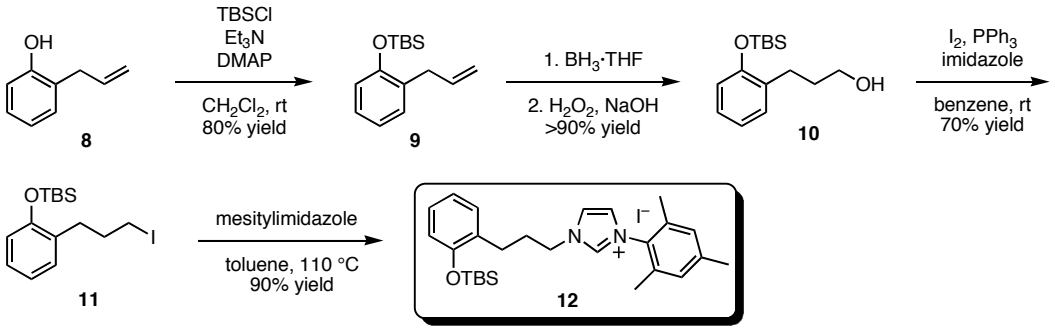


R_1 = substituted aryl ring, Me, CH_2-adamantyl
R_2 = H, 4-NO_2Ph, 6-Me-4-NO_2Ph.

Figure A2.1. Olefin metathesis catalysts bearing Schiff bases.

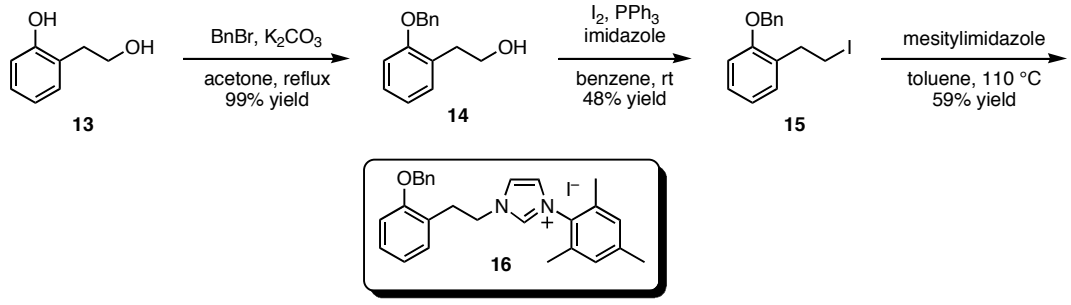
Results and Discussion

A variety imidazolium salts bearing one *N*-bound mesityl ring and one phenol were synthesized. The phenol was tethered to the imidazole ring through one, two, or three methylenes, or it was directly bound to a dihydroimidazole nitrogen atom. The synthesis of the three-methylene tethered phenol NHC precursor **12** is illustrated in Scheme A2.2. The hydroxyl group of 2-allylphenol (**8**) was protected as a TBS ether, and hydroboration/oxidation of the terminal olefin of **9** afforded **10**. The primary alcohol was converted to an alkyl iodide,[10] which reacted with mesitylimidazole to form imidazolium salt **12**.



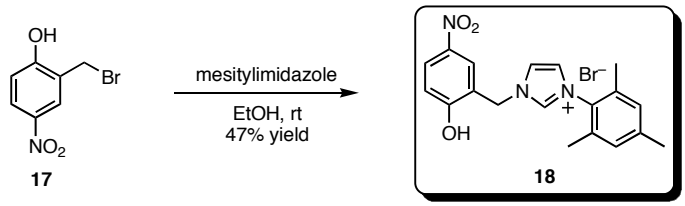
Scheme A2.2. Synthesis of three-methylene linker imidazolium salt.

The ligand with two methylene units separating the phenol from the imidazolium ring (**16**) was generated as shown in Scheme A2.3. The reaction of 2-hydroxyphenethyl alcohol (**13**) with benzyl bromide afforded benzyl ether **14**. As above, the primary alcohol was transformed into a primary alkyl iodide, which was displaced by mesitylimidazole.



Scheme A2.3. Synthesis of two-methylene linker imidazolium salt.

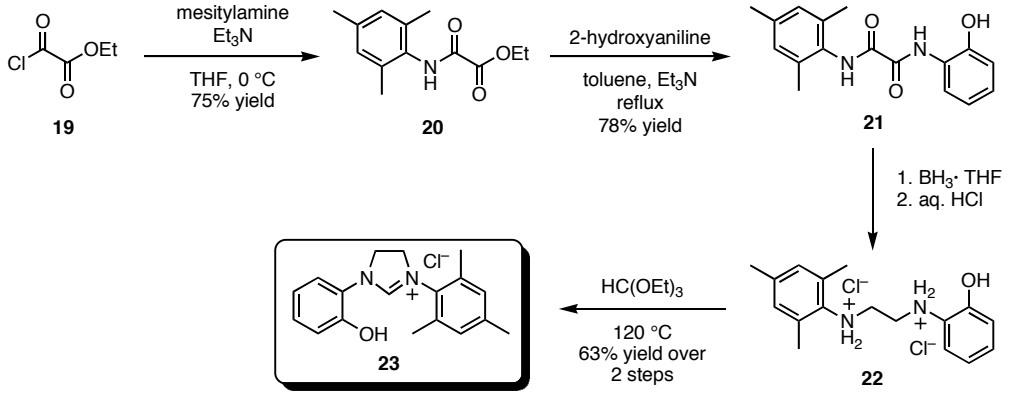
An imidazolium salt that had only one methylene separating the imidazole ring from the phenol (**18**) was made in one step from 2-hydroxy-5-nitrobenzyl bromide (**17**) (Scheme A2.4).



Scheme A2.4. Synthesis of one-methylene linker imidazolium salt.

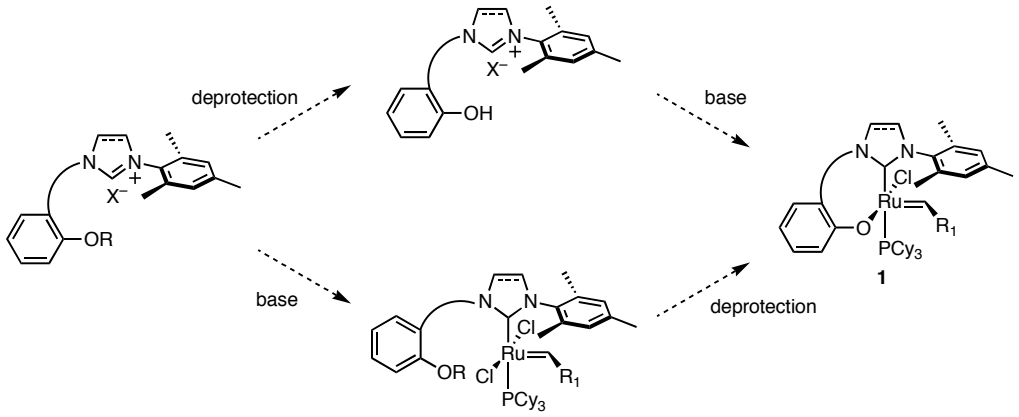
Finally, a compound where the phenol was directly bound to a dihydroimidazolium ring was synthesized (Scheme A2.5). This synthesis was originally developed by Dr. Andrew Waltman, a graduate student in the group at that time.[11] The unsymmetrical diamide **21** was made by first reacting mesitylamine with the acid chloride portion of **19** followed by amidation of the ethyl ester. It was reduced to the

diamine, which was converted to the HCl salt, and **22** was reacted with triethylorthoformate to afford **23**.



Scheme A2.5. Synthesis of unsymmetrical dihydroimidazolium salt.

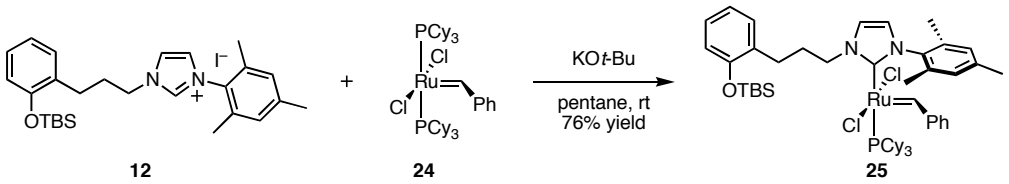
With the desired NHC precursors in hand, metal complexation was explored. Two approaches to accessing the ruthenium compounds were examined: substitution of an L-type ligand with a phenol-protected NHC followed by deprotection, and a one-step procedure where an NHC/phenoxide would replace both an L-type and a chloride ligand in one step (Scheme A2.6). In both case, two steps were needed starting from the phenol protected imidazolium salts.



Scheme A2.6. Two potential synthetic route to the ruthenium complexes.

Ligand substitution followed by phenol deprotection was explored first. When salt **12** was treated with potassium *t*-butoxide in the presence of ruthenium benzylidene

24, the desired mono-phosphine/mono-NHC complex **25** was isolated in 76% yield (Scheme A2.7). This complex displayed characteristic signals in the ^{1}H NMR (CD_2Cl_2) spectrum for mono-NHC Ru benzylidenes. A singlet at 19.2 ppm and a small doublet at 20.1 ppm ($J_{H,P}$ = 12.6 Hz) were present in the ^{1}H NMR spectrum, and a singlet at 34.4 ppm was present in the ^{31}P NMR spectrum. X-ray analysis of suitable crystals of **25** showed that the unsymmetrical NHC ligand was oriented so that the mesityl ring was positioned over the benzylidene phenyl ring (Figure A2.2). It is possible that the doublet at 20.1 ppm in the ^{1}H NMR spectrum arose from a rotamer of **25** where the alkyl chain was positioned over of the benzylidene. Complex **25** catalyzed the ring-closing metathesis reaction of diethyl diallylmalonate to >95% conversion within 30 min at rt.



Scheme A2.7. Synthesis of phenol-protected catalyst **25**.

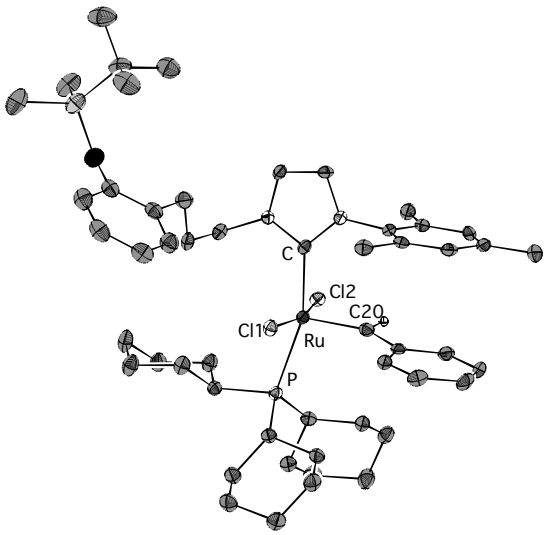


Figure A2.2. Structure of **25** with displacement ellipsoids drawn at 50% probability.

Complex **25** was treated with a variety of fluoride sources, but the TBS group was never removed. Attempts to make the ligand precursor **12** with a more labile TMS group were unsuccessful due to the instability of the trimethylsilyl ether. It was known that a benzyl protecting group could be removed from a hydroxyl located on a ligand bound to a ruthenium benzylidene,[12] so imidazolium salt **16** was reacted with base in the presence of the bisphosphine complex **24**. Unfortunately, pure product was never isolated from this reaction.

In order to avoid the hurdles associated with ruthenium-bound ligand deprotection, the one-step ligand substitution approach was explored. Many combinations of the ligands, ruthenium sources, and bases shown in Figure A2.3 were tested, but no new ruthenium alkylidenes were formed. These reactions were often solvent dependent, but the difference between solvents meant either no reaction occurred or the ruthenium source decomposed. During the course of these experiments, the Hoveyda group reported a chelating NHC-binaphthol ligand bound to a ruthenium alkylidene.[13] Silver carbonate was used as a base/NHC-transfer agent, so this was also attempted with the imidazolium salts in Figure A2.3. Either no reaction or complete decomposition of the ruthenium source occurred.

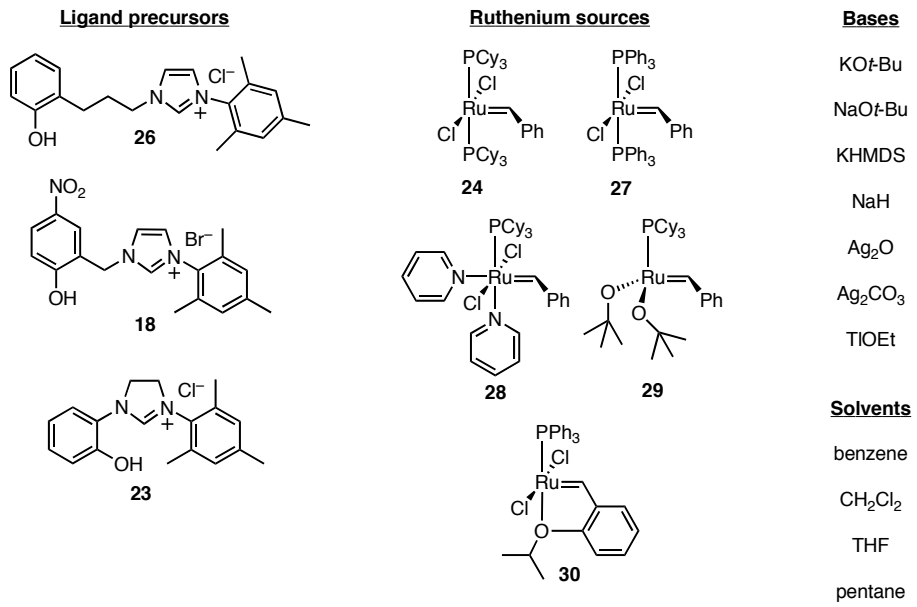
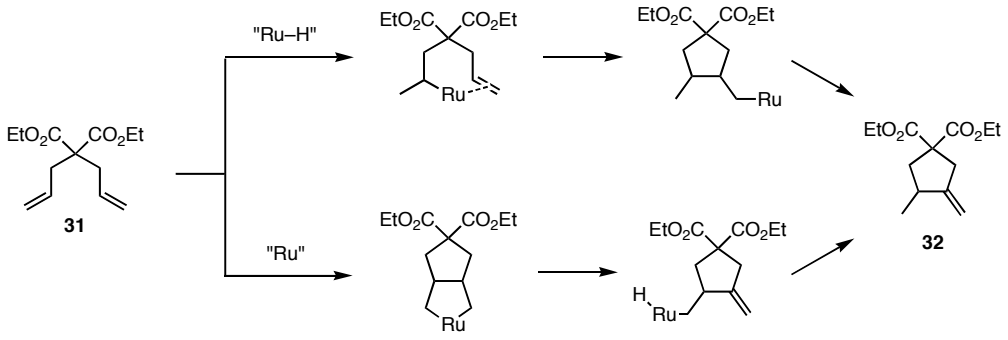


Figure A2.3. Failed attempts to synthesize NHC/phenol bindentate ruthenium complexes.

It was surprising that for many combinations, no reaction was observed. Upon treatment of the unprotected phenol/imidazolium salts with base, presumably both the phenol and the imidazolium were deprotected. Support for double deprotonation was supplied by the fact that, upon treatment with two equivalents of KHMDS, **23** bound to palladium as a bidentate ligand.[11] Because the phenoxide has a negative charge, a metal counterion from the base must be present. Complexation of the counterion by the phenoxide and the carbene could result in species that has low solubility and/or low reactivity to ligand substitution with the ruthenium sources in Figure A2.3. Therefore, compounds that are known to break up metal clusters were added: 18-crown-6, TMEDA, and HMPA.

A combination of **23**, **30**, KHMDS, and one of the additives in benzene-d_6 afforded a mixture of two new alkylidene peaks at 14.9 ppm (doublet, with a peak at 65.6 ppm in the ^{31}P NMR spectrum) and 17.8 ppm (singlet, with no corresponding peak in the ^{31}P NMR spectrum) in the ^{1}H NMR spectrum. Both peaks were present at the same

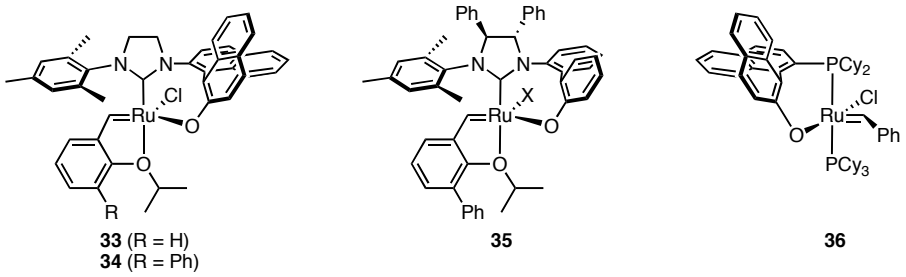
chemical shift regardless of what additive was used, so TMEDA (1 equiv relative to the ligand) was used in scale-up due to its low toxicity and ease of handling. The reactions were not clean, and although the two alkylidenes could be made separately based on reaction temperatures, the impure products never catalyzed the RCM of diethyl diallylmalonate.[14] A new alkylidene with a diagnostic singlet at 16.3 ppm in the ^{1}H NMR spectrum was generated by reacting **26** with **30**, KHMDS, and TMEDA. As with **23**, the reaction was not clean, and the impure ruthenium product did not catalyze the RCM of diethyl diallylmalonate at room temperature. On the other hand, after 21 h at 70 °C, no diethyl diallylmalonate (**31**) was present, but neither was the expected product. A five-membered ring bearing an exocyclic methylene (**32**) was generated either through a ruthenium hydride (Scheme A2.8, upper pathway) or a ruthenacyclopentane (Scheme A2.8, lower pathway). Other ruthenium species, including ruthenium alkylidenes, are known to catalyze this reaction.[15]



Scheme A2.8. Undetermined ruthenium species catalyzing non-metathesis ring closure.

The lack of success of this approach ultimately led to the termination of this project. The NHC/binaphthol complex **33** and other similar bidentate catalysts (**34** and **35**) made by the Hoveyda group were structurally similar to the complexes targeted in this study, and they were not highly metathesis active (Figure A2.4).[13a,16] Interestingly,

they catalyzed the ring-opening cross-metathesis (ROCM) of strained, cyclic alkenes with high *E*-selectivity (>98% *E*-isomer). For reasons that are not clear, catalyst **33**, **34**, and **35** are much more *E*-selective in ROCM than ruthenium catalysts bearing monodentate NHCs. Unfortunately, these complexes were not very active in reactions other than ROCM, such as the CM reaction of allyl benzene and 1,4-diacetoxy-*cis*-2-butene.[17] Additionally, I synthesized a phosphine variant (**36**)[18,19] of the complexes made in the Hoveyda group, but the RCM of diethyl diallylmalonate (**31**) only proceeded to 43% conversion, even at elevated temperatures.



33 (R = H)
34 (R = Ph)

35

36

Figure A2.4. Ruthenium alkylidene complexes bearing biphenyl and binaphthyl ligands.

Conclusion

A series of imidazolium/phenol salts were synthesized to be used as ligands on *Z*-selective ruthenium olefin metathesis catalysts. When the phenol was protected, ligand substitution occurred, and an active metathesis catalyst bearing an unsymmetrical NHC ligand was isolated. Unfortunately, attempts to remove the protecting group were unsuccessful. One-step phosphine/chloride substitution reactions were only achieved when TMEDA, HMPA, or 18-crown-6 were used, and even then the pure products were never isolated. The crude ruthenium alkylidenes did not catalyze RCM, and other structurally similar complexes were not efficient in CM, so no further exploration was

done. The structurally similar catalysts synthesized in the Hoveyda lab are highly *E*-selective in the ROCM of strained rings. An understanding of this selectivity could lend insight into the development of an *E*- or *Z*-selective olefin metathesis catalyst.

Experimental

General Information. All procedures using ruthenium compounds were carried out in a drybox or using Schlenk techniques. Organics were purchased from Aldrich, Alfa Aeser, or Acros and were used as received. Ruthenium compounds **24** and **27** were gifts from Materia. All solvents were purified by passage through activated A-2 alumina solvent columns and were degassed by bubbling through dry nitrogen. All flash chromatography was done using silica gel 60. ^{1}H NMR and ^{31}P NMR (121.388 MHz) spectral data was collected on a Varian Mercury 300 MHz instrument.

(2-Allylphenoxy)-*tert*-Butyldimethylsilane (9).[10] To 2-allylphenol (**8**) (2.0 g, 15 mmol), triethylamine (4.2 mL, 30 mmol), *t*-butyldimethylsilyl chloride (2.7 g, 18 mmol), and *N,N*-dimethylaminopyridine (0.18 g, 1.5 mmol) in a 250 mL round-bottom flask was added CH_2Cl_2 (40 mL). The solution was stirred at rt for 7h, washed with 50 mL brine, 50 mL water, and 50 mL brine. The organic layer was dried over Na_2SO_4 and evaporated to an oil. The product was purified by flash chromatography (100% *n*-pentane) to give 2.96 g (80% yield) of **9** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.05–7.16 (m, 2H), 6.89 (m, 1H), 6.80 (m, 1H), 5.91–6.05 (m, 1H), 5.00-5.08 (m, 2H), 3.38 (d, J = 6.6 Hz, 2H), 1.02 (s, 9H), 0.24 (s, 6H).

3-[2-(*tert*-Butyldimethylsilanyloxy)-Phenyl]-Propan-1-ol (10).[10] To **9** (2.8 g, 11 mmol) in a dry round-bottom flask was added THF (20 mL). The flask was cooled in an ice bath, and a 1M solution of BH_3-THF (11 mL) was added dropwise. After the reaction solution stirred at rt for 3 h, it was cooled in an ice bath. Distilled water (4.8 mL), 10% NaOH (4.8 mL) and 30% H_2O_2 (2.8 mL) were added to the reaction, and it stirred at 0 °C for 3 h. Aqueous HCl (5%) was added until pH 5 was reached, and the reaction mixture was extracted with ethyl ether (2 × 75 mL). The organic layers were combined and washed with saturated $NaHCO_3$ (2 × 30 mL) and brine (2 × 30 mL). It was dried over Na_2SO_4 and evaporated to 3.07 g of **10** as a colorless oil. The crude product was used directly in the next reaction. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.04–7.17 (m, 2H), 6.77–6.93 (m, 2H), 3.62 (t, J = 6.3 Hz, 2H), 2.69 (t, J = 7.6 Hz, 2H), 1.85 (m, 2H), 1.01 (s, 9H), 0.24 (s, 6H).

***tert*-Butyl-[2-(3-Iodopropyl)-Phenoxy]-Dimethylsilane (11).**[10] To crude **10** (1.5 g, 5.4 mmol), imidazole (0.93 g, 14 mmol), and triphenylphosphine (3.1 g, 12 mmol) in a dry round-bottom flask was added benzene (20 mL). The solution was cooled to 0 °C and iodine (2.8 g, 11 mmol) was added. After the solution stirred at rt 1.5 h, pentane (50 mL) was added and a yellow solid precipitated. The reaction mixture was filtered through Celite, and the filtrate was evaporated to a yellow oil. Purification by flash chromatography (100% pentane) afforded 1.43 g (70% yield) of **11** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.05–7.17 (m, 2H), 6.76–6.91 (m, 2H), 3.18 (t, J = 7.1 Hz, 2H), 2.69 (t, J = 7.4 Hz, 2H), 2.11 (apparent quintet, expected t of t, J = 7.4 Hz, 2H), 1.02 (s, 9H), 0.24 (s, 6H).

3-{3-[2-(*tert*-Butyldimethylsilanyloxy)-Phenyl]-Propyl}-1-(2,4,6-Trimethylphenyl)-3*H*-Imidazol-1-ium Iodide (12). To **11** (1.4 g, 3.8 mmol) and mesitylimidazole (0.84 g, 4.5 mmol) in a dry round-bottom flask was added toluene (10 mL). The solution stirred at 110 °C for 24 h. The mixture was cooled in an ice bath, and a tan solid precipitated. It was collected by suction filtration and was washed with ethyl ether to produce 1.91 g (90% yield) of **12** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 10.93 (apparent t, expected dd, J = 1.6 Hz, 1H), 7.46 (apparent t, expected dd, J = 1.6 Hz, 1H), 7.06–7.19 (m, 2H), 7.14 (apparent t, expected dd, J = 1.6 Hz, 1H), 6.99 (s, 2H), 6.76–6.92 (m, 2H), 4.70 (t, J = 7.4 Hz, 2H), 2.76 (t, J = 7.4 Hz, 2H), 2.34 (m, 2H), 2.33 (s, 3H), 2.08 (s, 6H) 1.00 (s, 9H), 0.23 (s, 6H).

3-[3-(2-Hydroxyphenyl)-Propyl]-1-(2,4,6-Trimethylphenyl)-3*H*-Imidazol-1-ium Chloride 26. To **12** (3.0 g, 5.3 mmol) was added ethanol (65 mL) and 2 N HCl (40 mL, 80 mmol). The solution stirred at rt for 14 h, and changed from colorless to orange. Approximately 2 g NaCl was added, and the solution stirred at rt for 24 h. It was neutralized with saturated $NaHCO_3$, and the ethanol was partially removed by evaporation. The solution was extracted with 2 × 150 mL CH_2Cl_2, and the organic layers were combined, dried over Na_2SO_4, and evaporated to an oil. The oil was placed under vacuum, and 1.9 g (99% yield) of **26** as a foamy solid formed. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 9.71 (apparent broad t, expected dd, 1H), 7.80 (m, 1H), 7.09–7.11 (m, 2H), 6.94–7.00 (m, 2H), 6.97 (s, 2H), 6.73–6.75 (m, 1H), 4.53 (t, J = 6.6 Hz, 2H), 2.62 (t, J = 7.1 Hz, 2H), 2.33 (s, 3H), 2.21–2.26 (m, 2H), 2.04 (s, 6H).

TBS-Phenol/NHC Ruthenium Benzylidene 25. Imidazolium salt **12** (1.03 g, 1.82 mmol), potassium *t*-butoxide (0.2 g, 1.82 mmol), and *n*-pentane (10 mL) were combined in a dry Schlenk flask. After stirring the mixture at rt for 2 h, **24** (1 g, 1.22 mmol) was added as a solid over 20 min. After stirring the resulting mixture for 14 h at room temperature, the pink reaction mixture was cooled to 0 °C and canula filtered. The maroon solid was washed with dry methanol, canula filtered, and dried by vacuum pump to afford 0.9 g (76% yield) of **25** as a maroon solid. Crystals suitable for X-ray diffraction were grown from benzene-pentane vapor diffusion. ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ 20.09 (d, J = 13 Hz, 1H)*, 19.20 (s, 1H), 6.70–8.10 (m, 7H), 7.86 (broad s, 2H), 6.30 (broad s, 2H), 4.77 (t, J = 7.5 Hz, 2H), 2.88 (t, J = 8.0 Hz, 2H), 2.40–2.55 (m, 2H), 2.34 (s, 3H), 1.93 (s, 6H), 0.95–1.93 (m, 33H), 1.07 (s, 9H), 0.28 (s, 6H). ^{31}P{^{1}H} NMR (CD_2Cl_2, ppm): δ 34.4 (s). MS (MALDI) 975.24, 977.23. CCDC Reference number 203038.

*This peak is present in the ^{1}H NMR spectrum of the X-ray quality material, and is presumably from the solution-phase rotomer of **25** where the alkyl chain of the NHC/phenol ligand is positioned above of the phenyl of the benzylidene.

2-(2-Benzyloxyphenyl)-Ethanol (14). To a dry round-bottom flask containing 2-hydroxyphenethyl alcohol (**13**) (4.2 g 30 mmol) and acetone (85 mL) was added K_2CO_3 (4.2 g 30 mmol) and benzyl bromide (3.6 mL, 30 mmol). The solution stirred at reflux for 4 h. It was then cooled to rt and stirred 12 h. The reaction mixture was filtered through Celite, and the filtrate was evaporated to a yellow oil. Purification by flash chromatography (20% ethyl acetate in hexanes) afforded 6.87 g (99% yield) of **14** as a

colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.30–7.46 (m, 5H), 7.17–7.24 (m, 2H), 6.90–6.96 (m, 2H), 5.09 (s, 2H), 3.86 (t, J = 6.3 Hz, 2H), 2.97 (t, J = 6.3 Hz, 2H).

2-(2-Benzyloxyphenyl)-Ethyl Iodide (15). To a solution of **14** (6.1 g, 27 mmol) in benzene (90 mL) at 0 °C was added imidazole (2.7 g, 40 mmol), triphenylphosphine (9.1 g, 35 mmol), and iodine (8.8 g, 35 mmol). The reaction solution stirred at rt for 2.5 h. Pentane (125 mL) was added, and a yellow precipitate formed. The mixture was filtered and the filtrate was evaporated to an oil. Purification by flash chromatography (100% pentane) afforde 4.3 g (48% yield) of **15** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.32–7.47 (m, 5H), 7.15–7.29 (m, 2H), 6.91–6.98 (m, 2H), 5.12 (s, 2H), 3.43 (t, J = 8.0 Hz, 2H), 3.28 (t, J = 8.0 Hz, 2H).

[2-(2-Benzyloxyphenyl)-Ethyl]-1-(2,4,6-Trimethylphenyl)-3*H*-Imidazol-1-ium Iodide (16). To **15** (4.3 g, 13 mmol) and mesitylimidazole (2.8 g, 15 mmol) was added toluene (35 mL). The reaction solution stirred at reflux 12 h, and the volatiles were removed. The remaining oil was purified by flash chromatography (2.5% MeOH in $CHCl_3$), and the product was placed under vacuum to provide 3.9 g (59% yield) of **16** as a pale yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 9.47 (br s, 1H), 7.20–7.50 (m, 7H), 6.81–7.12 (m, 4H), 6.97 (s, 2H), 5.14 (s, 2H), 4.95 (t, J = 6.6 Hz, 2H), 3.38 (t, J = 6.6 Hz, 2H), 2.33 (s, 3H), 1.94 (s, 6H).

3-(2-Hydroxybenzyl)-1-(2,4,6-Trimethylphenyl)-3*H*-Imidazol-1-ium Bromide (18). To a solution of 2-hydroxy-5-nitrobenzyl bromide (**17**) (2.0 g, 8.6 mmol) in ethanol

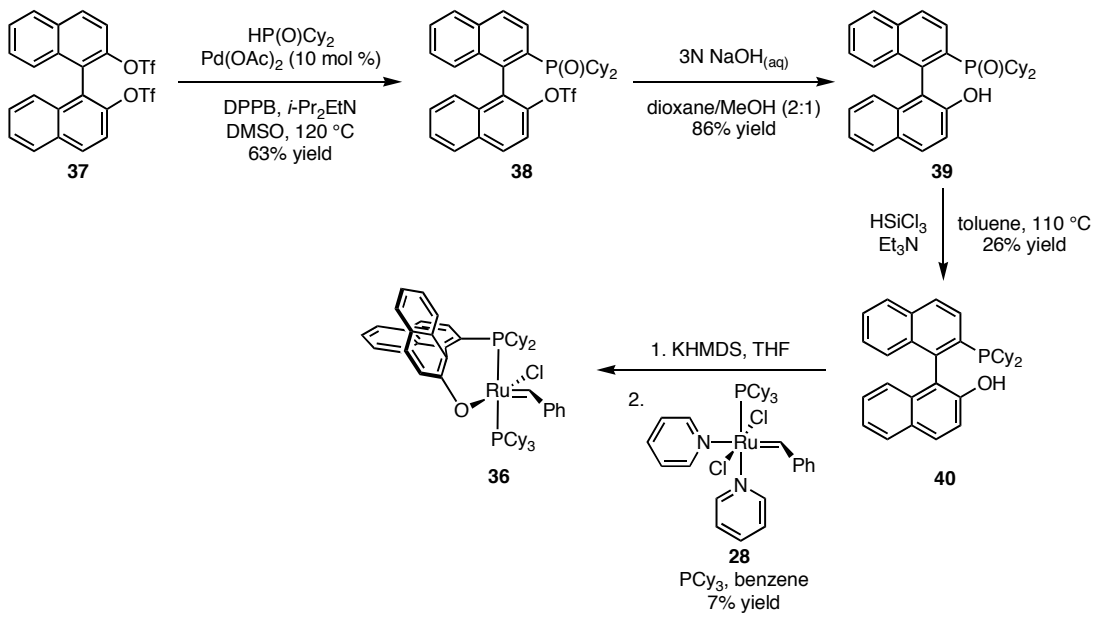
(20 mL) was added mesitylimidazole (1.9 g, 10 mmol). The reaction stirred at rt 1 h. A tan precipitate formed, and it was collected by suction filtration and was washed with ethyl ether to afford 1.7g (47% yield) of **18** as a tan solid. ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ 9.51 (apparent s, 1H), 8.36 (d, J = 2.7 Hz, 1H), 8.20 (dd, J = 8.8 Hz, 2.7 Hz, 1H), 8.02 (t, J = 1.6 Hz, 1H), 7.90 (t, J = 1.6 Hz, 1H), 7.13 (s, 2H), 7.06 (d, J = 8.8 Hz, 1H), 5.50 (s, 2H), 2.31 (s, 3H), 1.99 (s, 6H).

***N*-(2,4,6-Trimethylphenyl)-Oxalamic Acid Ethyl Ester (20).** To a solution of mesitylamine (5.2 mL, 37 mmol) and triethylamine (10.3 mL, 74 mmol) in THF (100 mL) at 0 °C was slowly added ethyl chlorooxoacetate (**19**) (4.1 mL, 37 mmol). After stirring at 0 °C for 3 h, ethyl acetate (50 mL) and 1 N HCl (100 mL) was added. The organic layer was removed, and the aqueous layer was extracted with 3 × 75 mL ethyl acetate. The combined organic layers were dried over Na_2SO_4 and evaporated to an oil. Upon hexanes addition, a white precipitate formed. The mixture was cooled in an ice bath, and 6.5 g (75% yield) of **20** as a white solid was collected by suction filtration. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.35 (br s, 1H), 6.93 (s, 2H), 4.44 (q, J = 7.1 Hz, 2H), 2.29 (s, 3H), 2.22 (s, 6H), 1.46 (t, J = 7.1 Hz, 3H).

***N*-(2-Hydroxyphenyl)-*N*'-(2,4,6-Trimethylphenyl)-Oxalamide (21).** To **20** (6.5 g, 28 mmol), *o*-hydroxyaniline (3.0 g, 28 mmol), and triethylamine (7.8 mL, 56 mmol) was added toluene (100 mL). The solution stirred at reflux for 17 h. After evaporating the solvent to a small volume, the reaction mixture was cooled in an ice bath. A solid precipitated and was collected by suction filtration. The solid was dissolved in ethyl

acetate (100 mL), and it was washed with 3 × 100 mL 1 N HCl. The organic layer was dried over Na_2SO_4 and was evaporated to afford 6.44 g (78% yield) of **21** as a tan solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 9.63 (br s, 1H), 8.79 (br s, 1H), 8.08 (br s, 1H), 7.04 (dd, J = 8.0, 1.6 Hz, 1H), 7.16–7.22 (m, 1H), 7.03 (dd, J = 8.1, 1.6 Hz, 1H), 6.92–6.98 (m, 1H), 6.96 (s, 2H), 2.32 (s, 3H), 2.24 (s, 6H).

3-(2-Hydroxyphenyl)-1-(2,4,6-Trimethylphenyl)-4,5-Dihydro-3*H*-Imidazol-1-ium Chloride (23). To **21** (1.0 g, 3.4 mmol) was added 1 M borane-THF (27 mL, 27 mmol), and the solution stirred at reflux for 12 h. The solution was cooled to rt, and 20 mL MeOH was added, followed by the addition of concentrated HCl until pH 1 was reached. The volatiles were evaporated until only a small volume was present. MeOH (50 mL) was added, and again the solvent was evaporated until only a small volume was present. This was repeated once more with MeOH, and once with EtOH until only a white precipitate was present. The solid (**22**) was collected via suction filtration, and 1.15 g was present. To the white solid **22** (1.15 g, ≤ 3.35 mmol) in a 50 mL round-bottom flask was added triethyl orthoformate (9.0 mL, 54.1 mmol). The mixture was stirred at 120 °C for 13 h, and a yellow precipitate formed. The mixture was cooled in an ice bath, and solid was collected by suction filtration. It was washed with cold hexanes to provide 0.67 g (63% yield) of **23** as a tan solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 8.89 (s, 1H), 7.63 (d, J = 8.0 Hz, 1H), 6.99–7.05 (m, 2H), 6.99 (s, 2H), 6.76–6.82 (m, 1H), 4.78 (t, J = 10.9 Hz, 2H), 4.36 (t, J = 10.9 Hz, 2H), 2.36 (s, 3H), 2.33 (s, 6H).



Trifluoromethanesulfonic Acid 2'-(Dicyclohexylphosphinoyl)-[1,1']-Binaphthal-enyl-2-yl Ester (38).[19] To racemic 1,1'-bi-2-naphthol bis(trifluoromethanesulfonate) (**37**) (5.0 g, 9.1 mmol), dicyclohexylphosphine oxide (3.9 g, 18.2 mmol), $Pd(OAc)_2$ (200 mg, 0.91 mmol), and 1,4-diphenylphosphinobutane (390 mg, 0.91 mmol) was added DMSO (35 mL) and triethylamine (6.3 mL, 36 mmol). The solution was heated to 120 °C for 15 h. Upon cooling, water (75 mL) was added, and the mixture was extracted with 3 × 150 mL ethyl acetate. The organic layers were combined, dried over $MgSO_4$, and evaporated to a yellow oil which was purified by flash chromatography (45:55 ethyl acetate/hexanes) to afford 3.5 g (63% yield) of **38** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.95–8.08 (m, 4H), 7.46–7.60 (m, 4H), 7.12–7.37 (m, 4H), 0.95–2.09 (m, 22H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 47.3 (s).

2'-(Dicyclohexylphosphinoyl)-[1,1']Binaphthalenyl-2-ol (39). To **38** (3.5 g, 5.8 mmol) was added dioxane (23 mL), methanol (11 mL) and 3 N NaOH (19.2 mL, 58 mmol). The

solution stirred for 14 h at rt, and changed from colorless to yellow. The acidity was lowered to pH 3 by concentrated HCl, and 50 mL water was added. The mixture was extracted with 3 × 100 mL CH_2Cl_2, and the organic layers were combined and evaporated to a white solid. The solid was suspended in a small amount of acetone, ethyl ether was added, and 2.4 g (86% yield) of **39** as a white solid was collected by vacuum filtration. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.69–8.02 (m, 5H), 7.44–7.53 (m, 2H), 7.04–7.28 (m, 4H), 6.52–6.55 (m, 1H), 0.42–2.21 (m, 22H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 50.7 (s).

2-(Dicyclohexylphosphino)-2'-Hydroxy-1,1'-Binaphthyl (40). To **39** (2.3 g, 5.0 mmol), toluene (80 mL), and triethylamine (23 mL, 170 mmol) in a dry, 200 mL round-bottom flask in an ice bath under N_2 was added trichlorosilane (4.2 mL, 41 mmol). The reaction mixture stirred under N_2 at 110 °C for 13 h. Upon cooling to rt, 80 mL ethyl ether and 10 mL saturated $NaHCO_3$ were carefully added. The mixture was filtered through Celite, washed with ether and toluene, and the filtrate was dried over Na_2SO_4 and evaporated to dryness. The residue was purified by flash chromatography (5% ethyl acetate in hexanes) to afford 0.58 g (26% yield) of **40** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.81–8.02 (m, 4H), 7.49–7.54 (m, 1H), 7.18–7.34 (m, 6H), 6.89–6.92 (m, 1H), 1.00–2.06 (m, 22H). ^{31}P{^{1}H} NMR ($CDCl_3$): δ –7.4 (s).

Phosphine/Hydroxy Binaphthyl Ruthenium Benzylidene (36). Phosphine/hydroxy binaphthyl ligand **40** (67 mg, 0.14 mmol) and KHMDS (28 mg, 0.14 mmol) were dissolved in THF (2 mL) in a dry Schlenk flask. After stirring 20 min at room temperature, the volatiles were removed by vacuum pump. Complex **28** (100 mg,

0.14 mmol), dissolved in benzene (5 mL), was added to the yellow residual solid. The yellow solid slowly dissolved, and after stirring 30 min at room temperature, PCy_3 (20 mg, 0.07 mmol) in benzene (2 mL) was added to the reaction mixture. The volatiles were removed after 5 min, and the solid residue was purified by flash chromatography (9:1 *n*-pentane/ethyl ether). The fractions containing the light brown band were evaporated to dryness, and the residue was dissolved in a minimum of ether. Pentane was added, the mixture was cooled in an ice bath, and the brown suspension was collected via suction filtration to afford 10 mg (7% yield) of **36** as a brown solid. ^{1}H NMR (300 MHz, C_6D_6, ppm): δ 20.29 (d, J = 4.4 Hz, 1H), 8.37 (d, J = 7.7 Hz, 2H), 6.80–7.96 (m, 15H), 1.00–2.40 (m, 55H). $^{31}P\{^{1}H\}$ NMR (C_6D_6) δ 47.8 (d, J = 230 Hz), 33.2 (d, J = 230 Hz).

X-ray Crystallographic Data

Complex	**25**
Empirical formula	$C_{52}H_{77}Cl_2N_2OPSiRu$
Formula weight	977.19
Crystal habit	Fragment
Crystal size	0.22 × 0.15 × 0.07 mm^3
Crystal color	Yellow
Diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Temperature	98(2) K
Unit cell dimensions	a = 13.6930(7) Å
	b = 13.8481(7) Å
	c =14.7461(8) Å
	α = 106.3870(10)°
	β = 106.6020(10)°
	γ = 92.7590(10)°
Volume	2545.4(2) $Å^3$
Z	2
Crystal system	Triclinic
Space group	P-1
Density (calculated)	1.275 Mg/m^3
Theta range	1.52 to 28.42°
h min, max	–18, 18
k min, max	–18, 18
l min, max	–19, 19
Reflections collected	53070
Independent reflections	11813
R_{int}	0.0704
GOF on F^2	1.136
Final R indicies [I>2σ(I)]	0.0354
Final weighted R [F_o^2]	0.0570

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[9] The rate-determining step in the initiation of Grubbs-type ruthenium catalysts is phosphine dissociation. If one of the L-type ligands does not dissociate, the complex is metathesis inactive. Because the imine is a weaker ligand than PCy_3, it is assumed that it would need to dissociate for the complex to enter a catalytic cycle. But because it is linked to the catalyst through the phenoxide, dissociation is not favorable. For more on catalyst initiation, see (a) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 3887–3897. (b) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543–6554.

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