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Stereoselective Formation of η^6-Arene Ruthenium(II) Complexes via Metal-Triggered Bergman and Hopf Cycloaromatizations

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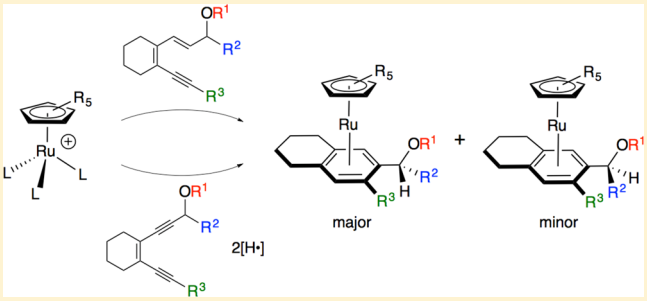
Supporting Information

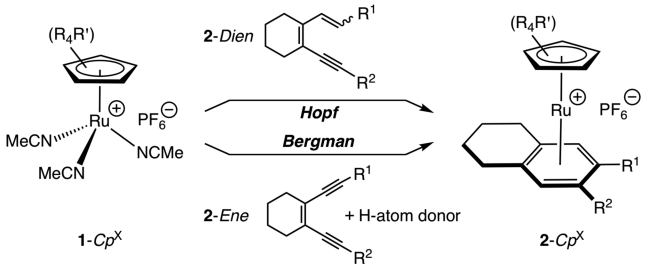
ABSTRACT: A stereoselective metal-mediated cycloaromatization of chiral conjugated dienynes and enediynes is described. For dienyne cycloaromatization, placement of the carbon stereocenter in the allylic position gives the highest diastereomeric ratios (dr). The observed stereoselectivity depends on the steric bulk of the alkyne substituent, as replacing a propargylic methyl for trimethylsilyl increases the dr from 56:44 to 80:20. For both enediyne and dienyne substrates, $[(\eta^5\text{-}C_5Me_5)Ru(NCMe)_3]PF_6$ exhibits greater diastereoselectivity than does $[(\eta^5\text{-}C_5H_5)Ru(NCMe)_3]PF_6$. For the same chiral enediyne substrate, $[(\eta^5\text{-}C_5Me_5)Ru(NCMe)_3]PF_6$ generates a 4:1 ratio of diastereomeric arene products, whereas both $[(\eta^5\text{-}C_5Me_4CF_3)Ru(NCMe)_3]PF_6$ and $[(\eta^5\text{-}C_5H_5)Ru(NCMe)_3]PF_6$ generate a 1:1 product mixture, indicative of a significant electronic influence of the ancillary ligand on diastereoselectivity. X-ray structure determination of several isolated ruthenium arene diastereomers confirms the assigned relative stereochemistry for the major and minor stereoisomeric metal arene products. Arene-binding experiments demonstrate that the observed stereoselectivity does not involve complexation of free arene by ruthenium.



INTRODUCTION

Cationic ruthenium(II) η^6-arene complexes are valuable auxiliaries for stereoselective processes and serve as activating groups for several difficult aromatic transformations (e.g., nucleophilic substitution, dearomatization, and aromatic CH lithiation).[1,2] Furthermore, half-sandwich ruthenium(II) complexes can trigger or promote challenging chemical transformations en route to η^6-arene complexes; we demonstrated previously the ability of $[(\eta^5\text{-}C_5R_4R')Ru(NCMe)_3]PF_6$ complexes (**1**-*Cp*, R = R′ = H; **1**-*Cp**, R = R′ = Me; **1**-*Cp*‡, R = Me, R′ = CF_3) to act as a metal trigger for the formal Bergman[3] and Hopf[4] cycloaromatization of enediynes **2**-*Ene* and dienynes **2**-*Dien*, respectively (Scheme 1).[5,6] In the case of six-π-electron substrates in which the benzenoid fragment is nonsymmetric (e.g., $R^1 \neq R^2$), cycloaromatization results in the formation of planar chiral sandwich complexes **2**-Cp^X, in which the $(\eta^5\text{-}Cp^X)Ru$ (Cp^X = Cp, Cp*, Cp‡) fragment can bind to either face of the benzannulated arene.[7]

Scheme 1. Cyclopentadienylruthenium-Triggered Hopf and Bergman Cycloaromatizations[5,6]



For **2**-*Dien* and **2**-*Ene*, incorporation of a stereocenter at either the allylic or propargylic position could potentially allow for stereoinductive addition of the $(\eta^5\text{-}C_5R_4R')Ru$ moiety, thus demonstrating diastereoselectivity in the course of a one-pot cycloaromatization/η^6-complexation reaction. Several methodologies exist to prepare chiral metal η^6-arene complexes with enhanced stereoselectivity from benzenoid precursors,[8,9] but few exist that work to both cycloaromatize acyclic precursors and complex a metal diastereoselectively. The most widely developed of these reactions is the Dötz benzannulation.[10] For example, Wulff and co-workers utilized chromium carbene **3** in combination with bulky, chiral propargylic ether **4**-*Alkyne* to give very high diastereomeric ratios in favor of $(CO)_3Cr(\eta^6\text{-arene})$ complex **4**-$Cr(CO)_3$ (Scheme 2).[10q] Since our initial report,[5] metal-triggered Bergman cyclizations have been further developed: for instance, Kündig reported the chromium-mediated cyclization of enediyne **5**-*Ene* to give the cycloaromatized complex **5**-$Cr(CO)_3$, which binds selectively to the least hindered face of an 11-membered enediyne ring.[11] This

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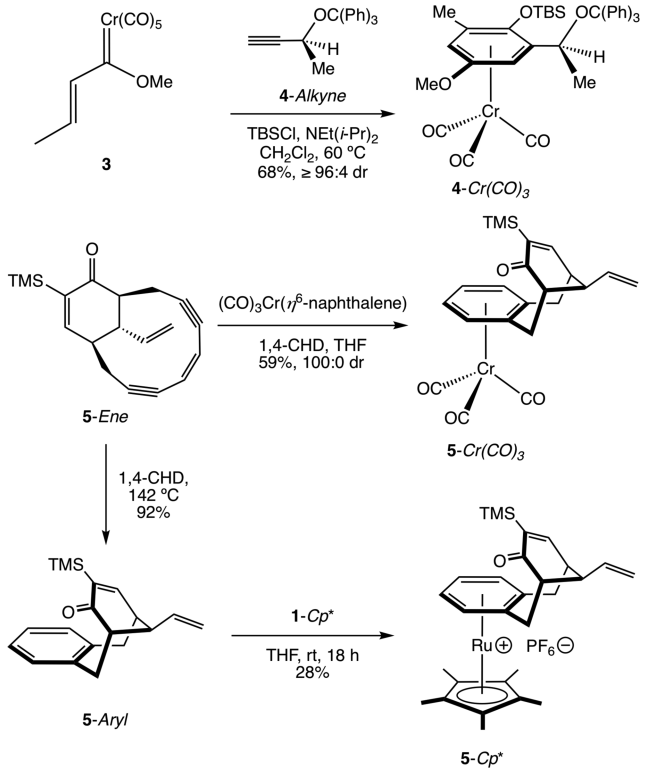
Scheme 2. Established Stereoselective Metal-Mediated Cycloaromatizations[10q11]

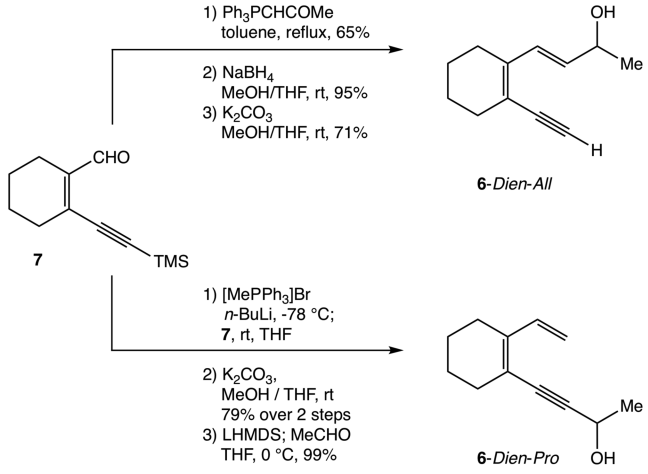


cycloaromatization was also triggered by ruthenium complex **1**-*Cp**, which gave a mixture of diastereomers. Alternatively, the preparation of **5**-*Aryl* by a thermal Bergman cyclization, followed by isolation and treatment with **1**-*Cp**, gave (η^5-C_5Me_5)Ru(η^6-arene) complex **5**-*Cp** in 28% yield as a single diastereomer. In each case, the cyclic nature of the substrate and the pendant spectator alkene substituent limit access to one face of the substrate, thereby enforcing a preference for metal binding. By utilizing a dienyne or enediyne substrate with a freely rotating stereocenter, we envisaged a stereochemical influence whereby the handedness of the chiral substituent would proscribe certain combinations of (η^5-Cp^X)Ru cation and substrate, resulting in pronounced diastereoselectivity. We herein report the first examples of facially selective metal η^6-arene binding by stereoinductive control of free rotors in metal-triggered Bergman and Hopf cycloaromatizations.

RESULTS AND DISCUSSION

Dienyne Stereoselectivity: Discovery and Substrate Scope. Dienynes **6**-*Dien-All* and **6**-*Dien-Pro* containing an allylic and propargylic stereocenter, respectively, were chosen as ideal starting points for initial reactivity studies due to their common precursor **7** (available in two steps from cyclohexanone)[12] and their expected convergent cycloaromatization with [(η^5-C_5Me_5)Ru(NCMe)$_3$]PF_6 (**1**-*Cp**) to afford the monosubstituted [(η^5-C_5Me_5)Ru(η^6-tetralin)]PF_6 complexes (**6**-*Cp**). Synthesis of both substrates commenced from TMS-substituted enynal **7** (Scheme 3). Wittig olefination of **7** followed by sodium borohydride reduction and desilylation gave the secondary allylic alcohol **6**-*Dien-All*. Similarly, olefination of **7** to the monosubstituted alkene followed by TMS deprotection yielded the terminal alkyne. This product

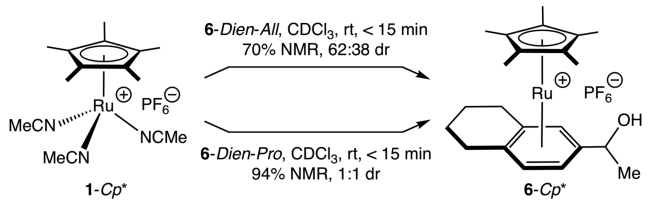
Scheme 3. Synthetic Route to Dienynes 6-*Dien-All* and 6-*Dien-Pro*



was then lithiated and quenched with acetaldehyde to give **6**-*Dien-Pro*.

When allyl-substituted dienyne **6**-*Dien-All* (24 μmol) was treated with a slight excess of **1**-*Cp** (37 μmol) in chloroform-*d* and monitored by ^{1}H NMR spectroscopy, immediate formation of two new (η^5-C_5Me_5)Ru complexes **6**-*Cp** was observed, with resonances at δ 1.86 and 1.88 (s, 15H). Cycloaromatization was suggested by the appearance of two corresponding sets of aryl resonances that integrated in a total 15:3 ratio with the respective Cp* signal in the ^{1}H NMR spectrum (δ 1.86:5.51 (d), 5.59 (d), and 5.85 (s); 1.88:5.50 (d), 5.57 (s), and 5.93 (d)). Integration relative to 1,3,5-tri-*tert*-butylbenzene as internal standard indicated the formation of **6**-*Cp** in 70% combined yield, with a diastereomeric ratio of 62:38 (Scheme 4

Scheme 4. Initial Observation of Stereoinduction in the Dienyne Cycloaromatization



and Table 1, entry 1). In contrast, reaction of the propargyl-substituted dienyne **6**-*Dien-Pro* (19 μmol) with **1**-*Cp** (28 μmol) proceeded under similar conditions to give **6**-*Cp** in 94% yield with no apparent stereoselectivity (entry 2). While both substrates gave **6**-*Cp** in good to excellent yield, only **6**-*Dien-All* with the stereocenter located in the allylic position was stereoselective.

Optimistic about the observed diastereomeric ratio, a series of dienynes with variable substitution were prepared (see the Experimental Section) and screened with **1**-*Cp** to investigate the requisite structural features for stereoselectivity (Table 1); further—informed by the initial observations with **6**-*Dien*—the target substrates all incorporate a 1-alkoxyalkyl stereocenter at the allylic position. Substrate **10**-*Dien* bearing a 1-methoxyethyl group at the allylic position and a methyl group at the propargylic position gave the highest observed diastereoselectivity (69:31 dr, entry 5), while the alcohol variant **8**-*Dien* gave a similar yield with slightly decreased selectivity (entry 3). In

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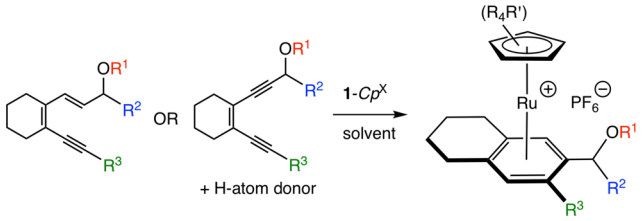
Table 1. Exploring Substrate Scope with Dienynes and Enediynes Containing a Stereocenter



entry[a]	substrate	product	R^1	R^2	R^3	solvent	time	yield, %/(dr)[b]
1	**6**-*Dien-All*	**6**-*Cp**	H	Me	H	$CDCl_3$	<15 min	70/(62:38)
2	**6**-*Dien-Pro*	**6**-*Cp**			1-(OH)Et	$CDCl_3$	<15 min	94/(50:50)
3	**8**-*Dien*	**8**-*Cp**	H	Me	Me	$CDCl_3$	<15 min	97/(64:36)
4	**9**-*Dien*	**9**-*Cp**	Et	Me	Me	$CDCl_3$	3.5 h	78/(63:37)[c]
5	**10**-*Dien*	**10**-*Cp**	Me	Me	Me	$CDCl_3$	<15 min	94/(69:31)
6	**11**-*Dien*	**11**-*Cp**	H	*i*-Pr	Me	$CDCl_3$	<15 min	44/(52:48)[d]
7	**12**-*Dien*		H	Me	TMS	$CDCl_3$	23 h	decomp
8	**8**-*Ene*	**8**-*Cp**	H	Me	Me	acetone-d_6	<15 min	87/(56:44)[e]
9	**12**-*Ene*	**12**-*Cp**	H	Me	TMS	acetone-d_6	<15 min	56/(80:20)[e,f]
10	**10**-*Dien*	**10**-*Cp*	Me	Me	Me	$CDCl_3$	<15 min	102/(58:42)
11	**12**-*Ene*	**12**-*Cp*	H	Me	TMS	acetone-d_6	>30 min	30/(50:50)[e]
12	**12**-*Ene*	**12**-*Cp*‡	H	Me	TMS	acetone-d_6	<15 min	32/(50:50)[g]

[a]Reactions run with 1.2−1.5 equiv of **1**-*Cp** at 0.02−0.006 M with respect to substrate with 1,3,5-tri-*tert*-butylbenzene as internal standard. [b]Yield and dr determined by ^{1}H NME. [c]Reaction stopped at 91% conversion of **9**-*Dien*; yield based on conversion. [d]Product was not isolated. [e]γ-terpinene as H-atom source. [f]Reaction tested in $CDCl_3$, acetone-d_6, THF-d_8, and acetone-d_6/THF-d_8 mixture with no effect on dr. [g]1,4-Cyclohexadiene as H-atom source.

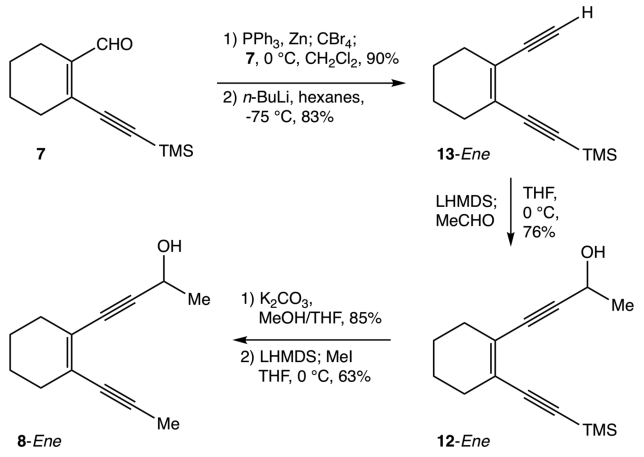
general, the reaction was adversely affected by increased steric bulk beyond a methyl substituent in any of the modified positions (entries 4, 6, and 7). While still diastereoselective, ethyl substitution at the alkoxy position slowed the cycloaromatization considerably (**9**-*Dien*; entry 4), whereas isopropyl substitution at the stereocenter did not retard the reaction but gave a much lower yield and essentially no stereoselectivity (**11**-*Dien*; entry 6). Finally, the trimethylsilyl-substituted dienyne **12**-*Dien* reacted with **1**-*Cp** but failed to form products **12**-*Cp** (entry 7).

Enediyne Stereoselectivity: Discovery and Substrate Scope. As a starting point for investigating the potential stereoselectivity of the ruthenium-triggered enediyne cycloaromatization reaction, we chose to prepare two cyclohexenediynes (**8**-*Ene* and **12**-*Ene*) containing a 1-hydroxyethyl stereocenter, while also varying the substitution at the other alkyne terminus. Common intermediate **7** was converted to the asymmetric enediyne **13**-*Ene* under Corey−Fuchs conditions (Scheme 5). Lithiation of **13**-*Ene* followed by quenching with acetaldehyde gave the TMS-substituted alcohol **12**-*Ene*, which was desilylated, lithiated, and quenched with methyl iodide to give the methyl-substituted alcohol **8**-*Ene*.

When a mixture of **12**-*Ene* (5 μmol) and **1**-*Cp** (8 μmol) with γ-terpinene (27 μmol) as H atom donor was dissolved in acetone-d_6 and monitored by ^{1}H NMR spectroscopy, immediate formation of two sets of resonances consistent with the product structure **12**-*Cp** were observed (Table 1, entry 9). Integration of the TMS resonances for the **12**-*Cp**-*maj* (δ 0.46) and **12**-*Cp**-*min* (δ 0.44) diastereomers in comparison to internal standard showed that the compounds formed in an 8:2 ratio in a combined NMR yield of 56%. Performing the reaction in chloroform-*d*, THF-d_8, or an acetone-d_6/THF-d_8 mixture showed no improvement in yield or dr.

Reaction of **8**-*Ene* (11 μmol) with **1**-*Cp** (16 μmol) under identical conditions (acetone-d_6; γ-terpinene 55 μmol) resulted in the formation of the previously isolated product **8**-*Cp** in comparably high yield (87% vs 97%) but with lower stereoselectivity (56:44 vs 64:32 dr; Table 1, entry 8 vs entry 3, respectively). Despite the low dr, the major and minor isomers of **8**-*Cp** formed are consistent for both the dienyne and enediyne cycloaromatization.

Scheme 5. Synthetic Route to Enediynes 8-*Ene* and 12-*Ene*



[(η^5-Cp^X)Ru(NCMe)$_3$]PF$_6$ Stereoselectivity: Assessing the Effect of the Metal−Ligand Environment. It was anticipated that the relative steric bulk and the electronic nature of the cyclopentadienyl ligand would have an effect on the selectivity of the dienyne and enediyne cyclizations. To probe the influence of the ancillary ligand environment, the best performing dienyne and enediyne were tested with unsubstituted [(η^5-C$_5$H$_5$)Ru(NCMe)$_3$]PF$_6$ (**1**-*Cp*). When dienyne **10**-*Dien* (6 μmol) was treated with **1**-*Cp* (9 μmol) in chloroform-*d*, cycloaromatization was observed to give products **10**-*Cp* in apparent 102% combined yield with a diastereomeric ratio of 58:42 (Table 1, entry 10), versus 94%

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yield and a 69:31 dr with **1**-*Cp** (entry 5). Cyclization of the enediyne substrate **12**-*Ene* (18 μmol) with **1**-*Cp* (20 μmol) in acetone-d_6, with γ-terpinene (90 μmol) as H atom donor, gave the expected products **12**-*Cp* in only 30% yield with no observed diastereoselectivity (entry 11), whereas the formation of **12**-*Cp** products with **1**-*Cp** proceeded to products in 56% yield with an 80:20 dr (entry 9). These results suggest that either the smaller steric size or the decreased electron-donating ability of the Cp ligand lowers the dr of both the dienyne and enediyne cycloaromatizations.

To better delineate whether the poor selectivity of **1**-*Cp* was a result of an electronic or a steric effect, [(η^5-$C_5Me_4CF_3$)Ru(NCMe)$_3$]PF_6 (**1**-*Cp*‡) was tested with enediyne **12**-*Ene*. Previous work by Gassman established the monotrifluoromethylated 1-trifluoromethyl-2,3,4,5-tetramethylcyclopentadienyl ligand (η^5-$C_5Me_4CF_3$, Cp‡) to be similar in electron-donating ability to the unsubstituted cyclopentadienyl ligand, while having a steric profile similar to the well-established pentamethylcyclopentadienyl ligand.[13] Cycloaromatization of **12**-*Ene* (20 μmol) with **1**-*Cp*‡ (21 μmol) and 1,4-cyclohexadiene (1,4-CHD, 42 μmol) as an H atom donor in acetone-d_6 afforded the corresponding **12**-*Cp*‡ diastereomers in a 1:1 ratio with a 36% combined yield (entry 12). The similar yield and lack of selectivity of **1**-*Cp* and **1**-*Cp*‡ with **12**-*Ene* suggests that, for this particular substrate, the electronic nature of the (Cp^X)Ru moiety exerted the predominant effect in determining the stereochemical outcome of enediyne cycloaromatization.

Solid-State Structure Determination of the [(η^5-Cp^X)Ru(η^6-tetralin)]PF_6 Products. The crystalline nature of the cationic cyclopentadienyl ruthenium arene complexes allowed for solid-state X-ray structure determinations on the major and minor diastereomers of **10**-*Cp** (Supporting Information) and **10**-*Cp* (Figure 1), as well as the minor diastereomers of **6**-*Cp** and **8**-*Cp** (Supporting Information). This analysis confirmed the diastereomeric relationship between the major and minor isomers and also showed a conserved stereochemical relationship between the carbon stereocenter and the planar chirality of the (η^5-C_5R_5)Ru(η^6-arene) binding for the major and minor diastereomers of each pair. In each case, the major stereoisomer has the smallest stereocenter substituent (hydrogen) directed toward the ortho position on the aromatic ring when the oxygen substituent is rotated syn with the metal fragment, as depicted in Figure 2.

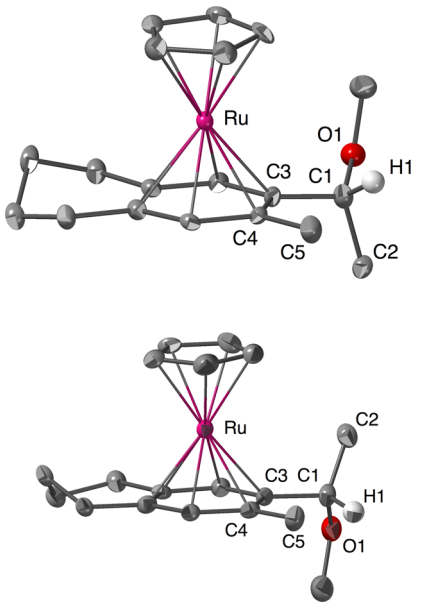


Figure 1. ORTEP drawings of the cations of **10**-*Cp-maj* (upper panel) and **10**-*Cp-min* (lower panel). The hexafluorophosphate anion and all hydrogen atoms except the stereocenter hydrogen at C1 are omitted for clarity.

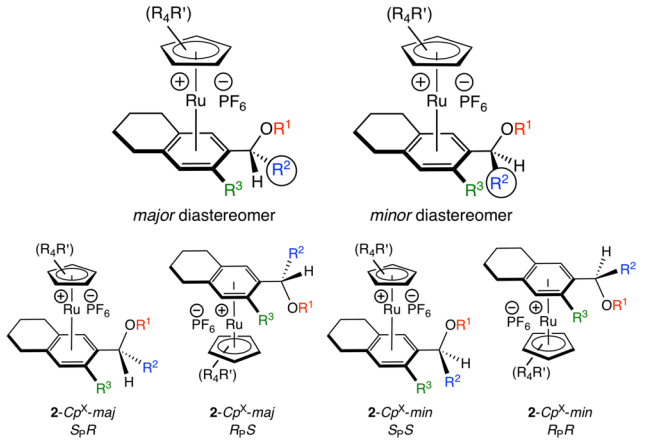
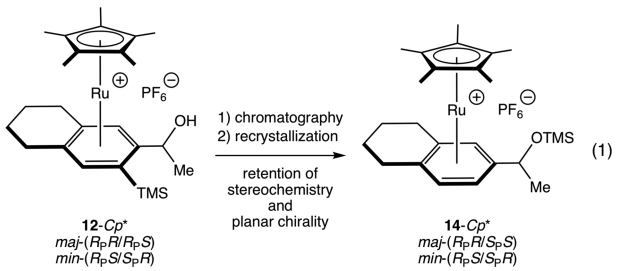


Figure 2. Generalized stereochemical model for predicting the major and minor stereoisomeric products of the dienyne and enediyne cycloaromatizations (upper panel). Generalized representations of the four stereoisomeric products from reaction of **1**-*Cp*^{X} with dienynes and enediynes (lower panel).

On a preparative scale, complex **12**-*Cp**-*maj* was isolated pure after repeated chromatography, but **12**-*Cp**-*min* proved unisolable due to a facile TMS migration to give the OTMS isomer **14**-*Cp**-*min* (eq 1). To establish the relative stereochemistry for complexes **12**-*Cp**, single-crystal samples grown from isolated **12**-*Cp**-*maj* and from a mixture of **12**-*Cp**-*min*/**14**-*Cp**-*min* were subjected to X-ray crystallographic analysis. In both cases, the solid-state structures obtained were of the TMS-migrated products, **14**-*Cp**-*maj* and **14**-*Cp**-*min*. It is unclear if the isomerizations of **12**-*Cp** to **14**-*Cp** are intra- or intermolecular, but regardless of the mechanism, it is highly unlikely that the TMS migration affects either the carbon stereocenter or the planar chirality of the metal fragment, and the stereochemical assignments of **12**-*Cp**-*maj* and **12**-*Cp**-*min* are inferred to correlate with **14**-*Cp**-*maj* and **14**-*Cp**-*min*, respectively.



Arene-Binding Experiments. Two basic mechanisms can be envisioned for the stereoselective dienyne and enediyne cycloaromatizations: (i) the metal remains coordinated to the substrate throughout the reaction and is bound stereoselectively as a consequence of the cyclization or (ii) the metal catalytically

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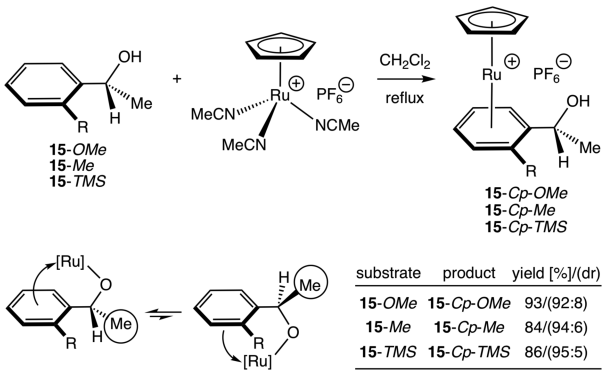
cyclizes the substrate and then binds stereoselectively to the newly formed arene in a subsequent step.

Uemura and co-workers have demonstrated the facially selective binding of chiral, ortho-substituted benzylic alcohols (**15**) with **1**-*Cp* to form (η^5-C_5H_5)Ru(η^6-arene) complexes **15**-*Cp* (Scheme 6).[9] The stereoselectivity of these reactions was

Scheme 6. Stereoselective (η^5-C_5H_5)Ru(η^6-arene) Complexation of Chiral, Ortho-Substituted Benzylic Alcohols[9]



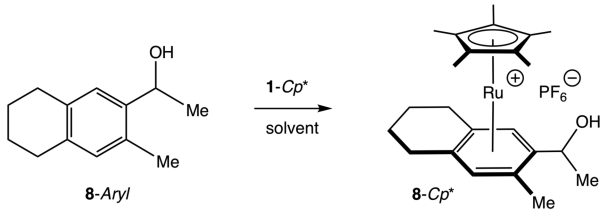
rationalized by a proposed precomplexation equilibrium with the hydroxy substitutent, whereby facial selectivity of the arene is enforced by minimizing steric interactions between the ortho and stereocenter substituents of the arene. Although not a direct comparison, binding of the Uemura substrates appears to occur with *greater* stereoselectivity (dr >92:8 in all cases; Scheme 6, inset) in comparison to that observed for the dienyne and enediyne substrates in this study, suggesting an alternative binding mechanism.

To distinguish between the two η^6-complexation mechanisms, an arene-binding experiment was performed in which 6-(1-hydroxyethyl)-7-methyltetralin (**8**-*Aryl*)—the arene formed from cyclization of **8**-*Dien* or **8**-*Ene*—was bound by reaction with **1**-*Cp** to give η^6-arene complexes **8**-*Cp** (Table 2). Substrate **8**-*Aryl* is readily accessible by sodium borohydride reduction of commercially available 6-acetyl-7-methyltetralin. Reaction of arene **8**-*Aryl* (34 μmol) with **1**-*Cp** (51 μmol) under dienyne cyclization conditions ($CDCl_3$; no H atom source) resulted in slow complexation (70 h; 48% conversion) to form **8**-*Cp** in excellent yield (99%) and diastereomeric ratio (85:15) (Table 2, entry 1). Subjecting **8**-*Aryl* (11 μmol) to enediyne cyclization conditions (acetone-d_6; γ-terpinene, 55 μmol; **1**-*Cp**, 16 μmol) resulted in rapid formation of **8**-*Cp** (entry 2) but in low conversion, as γ-terpinene competed with the arene for binding of **1**-*Cp**, resulting in the formation of [(η^5-C_5Me_5)Ru(η^6-*p*-cymene)]PF_6 from the dehydrogenation of γ-terpinene. Performing the reaction without γ-terpinene (**8**-*Aryl*, 11 μmol; **1**-*Cp**, 16 μmol; entry 3) resulted in a similar yield and dr, with high conversion of **8**-*Aryl*. In all cases the major and minor diastereomeric products are spectroscopically consistent with those formed from the cyclization reactions and, most importantly, binding of the free arene with **1**-*Cp** resulted in a significantly *higher* stereoselectivity than the reactions of **1**-*Cp** with dienyne **8**-*Dien* or enediyne **8**-*Ene*, suggesting that binding scenario ii is inoperative.

Computational Analysis of the Diastereomeric Ruthenium Arene Complexes. In order to address the relative thermodynamic stabilities of the diastereomeric ruthenium arene products, BP86/Def2-TZVPP calculations were undertaken on **10**-*Cp-maj*, **10**-*Cp-min*, **10**-*Cp*-maj*, and **10**-*Cp*-min* (Figure 3 and Table S9 in the Supporting Information). The calculated 2.7 kcal/mol energy difference between **10**-*Cp-maj* and **10**-*Cp-min* is nearly identical with the 2.8 kcal/mol energy difference between **10**-*Cp*-maj* and **10**-*Cp*-min*. In both cases, the lower energy diastereomer corresponds to the major isomer formed experimentally (Table 1, entries 5 and 10). This substantial energy difference indicates that a thermodynamic product ratio for two arene diastereomers in each pair would have been >120:1.

For both pairs of arene diastereomers the Ru−arene(centroid) distance is shorter for the major isomer than for the minor isomer. This contrasts with the Ru−Cp(centroid) and Ru−Cp*(centroid) distances, which are nearly identical in the four complexes (1.832−1.834 Å). The major diastereomers in each set have C2−C1−C3−Ru torsion angles of 179.7° (**10**-*Cp-maj-calc*) and 178.8° (**10**-*Cp*-maj-calc*), which places the methyl substituent distal to ruthenium. In the minor diastereomers these torsion angles are 11.8° (**10**-*Cp-min-calc*) and −78.8° (**10**-*Cp*-min-calc*), thereby placing the C2 methyl proximal to ruthenium. In methoxycyclohexane the equatorial isomer is 0.75 kcal/mol more stable than the axial isomer, whereas for methylcyclohexane that energy difference is 1.70 kcal/mol. Thus, the positioning of the C2 methyl relative to ruthenium appears to significantly influence the relative stabilities of the major and minor diastereomers.

Table 2. Arene-Binding Experiments



entry[a]	arene conversion, %	H atom donor	solvent	time	yield, %/(dr)[b]
1	48	solvent	$CDCl_3$	70 h	99/(85:15)
2	36	γ-terpinene	acetone-d_6	<50 min	99/(87:13)[c]
3	95	solvent	acetone-d_6	<50 min	91/(81:19)

[a]Reactions run with 1.5 equiv of **1**-*Cp** at 0.02−0.06 M with respect to substrate with 1,3,5-tri-*tert*-butylbenzene as internal standard. [b]Yield and dr determined by ^{1}H NMR. [c]Accompanied by formation of [(η^5-C_5Me_5)Ru(η^6-*p*-cymene)]PF_6.

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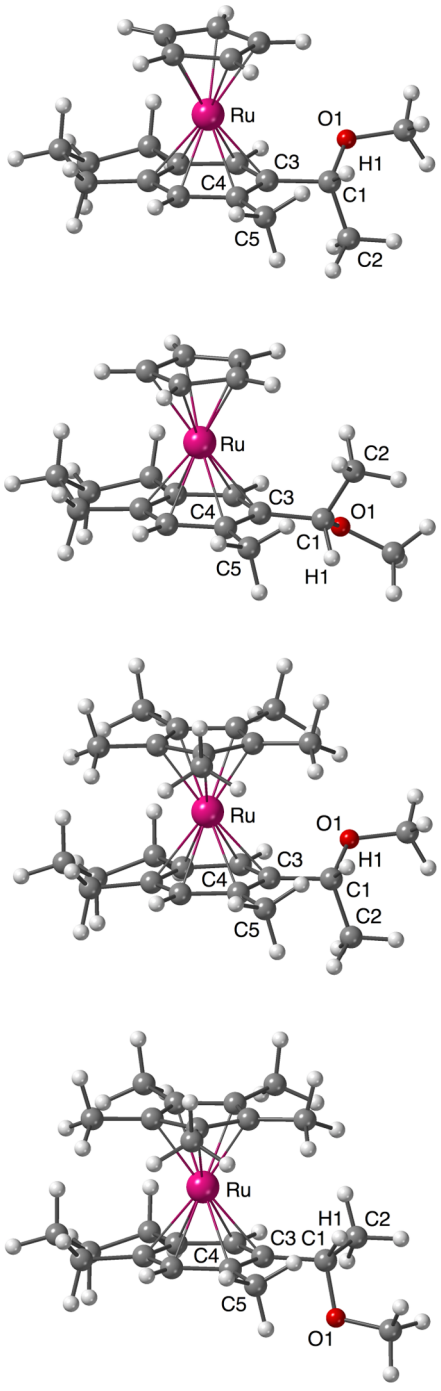

Figure 3. From top to bottom, calculated structures for cations of **10**-*Cp-maj-calc*, **10**-*Cp-min-calc*, **10**-*Cp*-maj-calc*, and **10**-*Cp*-min-calc*.

CONCLUSION

In summary, we have demonstrated the first examples of stereoselective metal η^6-arene complexation for ruthenium(II)-mediated cycloaromatization of chiral dienynes and enediynes that contain freely rotating stereocenters. We have identified (1) several important structural features of the metal system and substrate needed for stereoinduction, (2) a consistent relative stereochemistry of the major and minor diastereomeric products for both the dienyne and enediyne cycloaromatizations, (3) the importance of ancillary ligand electronic effects on diastereoselectivity, and (4) arene-binding experiments which suggest that the diastereoselectivity does not arise from simple complexation of the benzenoid product. Future studies will be focused toward developing a mechanistic model to account for the stereoselectivity, as well as identification of metal/ligand systems that proceed with higher diastereoselectivity.

EXPERIMENTAL SECTION

General Information. All manipulations were carried out under an atmosphere of dry dinitrogen using standard Schlenk or glovebox techniques. NMR-scale ruthenium cyclization reactions were performed under a dry dinitrogen atmosphere in 5 mm J. Young style NMR tubes equipped with a Teflon needle-valve adapter using freshly degassed solvents (freeze/pump/thaw procedure). Chloroform-*d* was dried and stored over calcium hydride under a dinitrogen atmosphere. Acetone-d_6 was dried over freshly activated 4 Å molecular sieves for 5 h under a dinitrogen atmosphere before transfer *in vacuo* to a separate Straus flask. Toluene, hexanes, diethyl ether, methylene chloride, and tetrahydrofuran were dried on columns of activated alumina using a J. C. Meyer (formerly Glass Contour) solvent purification system. Methanol was purchased as the anhydrous DriSolv from Sigma-Aldrich and used as received. $[(\eta^5\text{-}C_5Me_5)Ru(NCMe)_3]PF_6$ was synthesized according to the literature procedure.[14] All other literature compounds were prepared according to the indicated reference or were purchased from commercial suppliers and used as received. Preparative thin-layer chromatography (PTLC) was performed using glass plates precoated with silica gel (1 mm, 60 Å pore size, EMD Chemicals) and visualized by exposure to ultraviolet light. Flash column chromatographic purification of synthetic intermediates and substrates was performed using silica gel (60 Å, particle size 43−60 μm, 230−400 mesh, EMD Chemicals), activated neutral Brockmann Activity grade I (150 mesh, Sigma-Aldrich), or reverse-phase octadecylsilane bonded to silica gel (particle size 40 μm, 60 Å, J. T. Baker).

Instrumentation. NMR spectra were recorded on Varian Mercury 300 (^{1}H, 300 MHz; ^{13}C 75.5 MHz), Varian Mercury 400 (^{1}H, 400 MHz; ^{13}C 100.7 MHz), Jeol ECA 500 (^{1}H, 500 MHz), and Varian VX 500 (^{1}H, 500 MHz; ^{13}C 125 MHz) spectrometers. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (^{1}H and ^{13}C, δ 0.00 ppm), with reference to the residual proton or carbon resonance for $CDCl_3$ (^{1}H, δ 7.26 ppm; ^{13}C δ 77.16 ppm) or acetone-d_6 (^{1}H, δ 2.05 ppm; ^{13}C, δ 29.84 ppm). Infrared (IR) spectra were recorded on a Nicolet Avatar 360 FT-IR instrument with KBr or NaCl plates as thin films or JASCO FT-IR 4100 attenuated total reflectance (ATR) platform (3 mm) using ZnSe plates (thin films). High-resolution mass spectra were obtained by the University of California, San Diego Mass Spectrometry Facility. Melting points are uncorrected and were recorded on a Stanford Research Systems EZ-Melt apparatus.

Computation. The structural and energetic analyses of the molecular systems described in this study were carried out using the BP86 density functional,[15,16] with an ultrafine grid, together with the Def2-TZVPP basis set.[17] The effects of solvent were included using the continuum solvation model, COSab, on the basis of the original theory of Klamt modified for ab initio theory,[18,19] with a dielectric for trichloromethane. Full geometry optimizations were performed and uniquely characterized via second derivative (Hessian) analysis to establish stationary points and effects of zero point energy and thermal corrections. Visualization and analysis of structural results were carried out using Avogadro.[20]

(*E*)-4-(2-Ethynylcyclohex-1-enyl)but-3-en-2-ol (6-*Dien-All*). $NaBH_4$ (25 mg, 0.662 mmol) was added to a stirred solution of 7 (102 mg, 0.414 mmol) in MeOH/THF (4 mL, 1:1). After 10 min of stirring at 23 °C, anhydrous K_2CO_3 (171 mg, 1.24 mmol) was added. After 16 h of stirring at 23 °C, the reaction mixture was then diluted with water (8 mL) and extracted with Et_2O. The organic extract was washed with brine (4 mL), dried over $MgSO_4$, concentrated, and purified by PTLC (8/2 hexanes/EtOAc) to afford **6**-*Dien-All* as a peach solid (52 mg, 71% yield). Mp: 41−43 °C. IR (KBr, thin film): 3299 (s, $C_{sp}H$), 2084 (C≡C) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (d, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.57−1.69 (m, 4H, 4,5-CH_2), 1.70 (s,

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1H, OH), 2.19−2.30 (m, 4H, 3,6-CH_2), 3.25 (s, 1H, C≡CH), 4.42 (p, $^3J_{HH}$ = 7 Hz, 1H, C(*H*)OH), 5.79 (dd, $^3J_{HH}$ = 16 Hz, 7 Hz, 1H, CH=C*H*C(H)OH), 6.94 (d, $^3J_{HH}$ = 16 Hz, 1H, C*H*=CHC(H)OH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 22.1 (CH_2), 22.3 (CH_2), 23.5 (CH_2), 25.2 (CH_2), 30.8 (CH_3), 69.3 (C(H)OH), 82.3 (C≡CH), 83.8 (C≡CH), 119.0 (C=C), 129.8 (CH=CH), 133.6 (CH=CH), 141.3 (C=C). HRMS-(EI) (*m*/*z*): $[M + H]^+$ calcd for $C_{12}H_{16}O$, 176.1196; found, 176.1194.

4-(2-Vinylcyclohex-1-en-1-yl)but-3-yn-2-ol (6-*Dien-Pro*). A 2.5 M solution of *n*-BuLi (0.940 mL, 2.34 mmol) in hexanes was added to a stirred heterogeneous mixture of $[MePPh_3]Br$ (836 mg, 2.34 mmol) in THF (78 mL) at −78 °C. The resulting yellow solution was warmed to 23 °C, and a solution of **7** (303 mg, 1.47 mmol) in THF (3.8 mL) was added over 15 min. After it was stirred at 23 °C for 2 h, the reaction mixture was poured over saturated aqueous NH_4Cl (150 mL) and extracted with Et_2O (200 mL). The organic extracts were washed with brine (150 mL), dried over Na_2SO_4, concentrated, and purified by flash column chromatography (silica gel, 99/1 hexanes/EtOAc) to afford the TMS-substituted dienyne as a clear oil. Anhydrous K_2CO_3 (610 mg, 4.41 mmol) was added to a stirred solution of the resulting product in MeOH/THF (15 mL, 1/1) at 23 °C. After 4 h of stirring at 23 °C, the reaction mixture was filtered through a fritted funnel, concentrated, diluted with aqueous 1 M HCl (30 mL) and extracted with Et_2O (30 mL). The organic extracts were washed with 1 M HCl (20 mL), water (20 mL), and brine (20 mL), dried over $MgSO_4$, concentrated, and purified by flash column chromatography (silica gel, 99/1 hexanes/EtOAc) to afford the terminal alkyne as a clear oil (153 mg, 1.16 mmol). A 1 M solution of LiHMDS (3.47 mL, 3.47 mmol) in THF was added to a stirred solution of the resulting product in THF (12 mL) at 0 °C. After the mixture was stirred at 0 °C for 30 min, acetaldehyde (0.325 mL, 5.80 mmol) was added. After this mixture was stirred at 0 °C for 30 min, the reaction mixture was poured over saturated aqueous NH_4Cl (30 mL) and extracted with Et_2O (30 mL). The organic extracts were washed with brine (30 mL), dried over $MgSO_4$, concentrated, and purified by flash column chromatography (silica gel, 8/2 hexanes/EtOAc) to afford **6**-*Dien-All* as a clear oil (76 mg, 29% yield over three steps). IR (NaCl, neat): 3332 (OH), 2208 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.51 (d, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.57−1.71 (m, 4H, 4,5-CH_2), 1.76−1.81 (m, 1H, OH), 2.19−2.29 (m, 4H, 3,6-CH_2), 4.67−4.77 (m, 1H, C(*H*)OH), 5.09 (d, $^3J_{HH}$ = 11 Hz, 1H, CH=C(H_{cis})H), 5.25 (d, $^3J_{HH}$ = 17.5 Hz, 1H, CH=C(H_{trans})H), 7.05 (dd, $^3J_{HH}$ = 17.5 Hz, 11 Hz, 1H, C*H*=CH_2). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 22.1 (CH_2), 22.4 (CH_2), 24.5 (CH_2), 24.8 (CH_2), 30.9 (CH_3), 59.1 (CH(OH)), 84.1 (C≡C), 96.1 (C≡C), 113.3 (CH=CH_2), 119.4 (C=C), 136.9 (*C*H=CH_2), 140.9 (C=C). HRMS-(EI) (*m*/*z*): $[M + H]^+$ calcd for $C_{12}H_{16}O$, 176.1196; found, 176.1195.

General Procedure for Dienyne and Enediyne Cyclization Reactions and Arene-Binding Experiments. Dienyne, enediyne, or arene substrate and 1,3,5-tri(*tert*-butyl)benzene (0.5−1 mg) were added to a J-Young style NMR tube fitted with a Teflon needle-valve adapter. In the case of enediyne substrates, an H atom donor (γ-terpinene or 1,4-CHD) was also added. The J-Young NMR tube was evacuated on a high-vacuum Schlenk line, and deuterated solvent was transferred *in vacuo* with standard Schlenk techniques. An initial NMR experiment was conducted to establish relative ratios of starting material to internal standard. In an inert-atmosphere glovebox the J-Young NMR tube was uncapped, ruthenium complex **1**-Cp^X was added to the reaction solution, recapped, and immediately analyzed by NMR spectroscopy. Additional NMR experiments were conducted, if necessary, until complete consumption of dienyne, enediyne, or arene starting materials.

(η^5-Pentamethylcyclopentadienyl)(η^6-6-(1-hydroxyethyl)-tetralinyl)ruthenium(II) Hexafluorophosphate (6-*Cp).** After 30 min at 23 °C, the NMR scale reaction mixture of **6**-*Dien-Pro* with **1**-*Cp** was concentrated and purified by flash column chromatography (alumina, 95:5 CH_2Cl_2/acetone) followed by crystallization (CH_2Cl_2/Et_2O) to afford a mixture of **6**-*Cp*-maj* and **6**-*Cp*-min* as a colorless solid (4.2 mg, 31% yield). **6**-*Cp*-maj* and **6**-*Cp*-min* were isolated after repeated alumina chromatography. (**6**-*Cp*-maj*): Mp. (dec) 236−239 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 1.55 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH(OH)CH_3), 1.86 (s, 15H, Cp*), 1.59−1.94 (m, 4H, 2,3-CH_2), 2.31−2.46 (m, 3H, 1,4-CH_{syn}, OH), 2.66−2.88 (m, 2H, 1,4-CH_{anti}), 4.57 (dq, $^3J_{HH}$ = 6.5 Hz, 4.5 Hz, 1H, C*H*(OH)CH_3), 5.51 (d, $^3J_{HH}$ = 6 Hz, 1H, 7/8-C_{Ar}H), 5.59 (dd, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, 1H, 7/8-C_{Ar}H), 5.85 (s, 1H, 5-C_{Ar}H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 10.2 (CpCH_3), 21.9 (2 × CH_2), 26.0 (CH_2), 26.1 (CH_2), 27.1 (CH(OH)CH_3), 66.7 (*C*H(OH)CH_3), 83.2 (C_{Ar}H), 83.9 (C_{Ar}H), 86.4 (C_{Ar}H), 95.0 (Cp*), 100.8 (C_{Ar}), 101.1 (C_{Ar}), 108.0 (C_{Ar}). HRMS-(EI) (*m*/*z*): $[M + H]^+$ calcd for $C_{22}H_{31}ORu.F_6P$, 407.1445; found, 407.1453. (**6**-*Cp**-*min*): Mp. (dec) 254−258 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 1.55 (d, $^3J_{HH}$ = 6 Hz, 3H, CH(OH)CH_3), 1.88 (s, 15H, Cp*), 1.61−1.92 (m, 4H, 2,3-CH_2), 2.36−2.47 (m, 2H, 1,4-CH_{syn}), 2.53 (d, $^3J_{HH}$ = 5 Hz, 1H, OH), 2.70−2.82 (m, 2H, 1,4-CH_{anti}), 4.59 (qd, $^3J_{HH}$ = 6 Hz, 5 Hz 1H, C*H*(OH)CH_3), 5.50 (d, $^3J_{HH}$ = 6 Hz, 1H, 7/8-C_{Ar}H), 5.57 (s,1H, 5-C_{Ar}H), 5.93 (d, $^3J_{HH}$ = 6 Hz, 1H, 7/8-C_{Ar}H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 10.3 (CpCH_3), 21.76 (CH_2), 21.83 (CH_2), 25.8 (CH_2), 26.3 (CH_2), 27.1 (CH(OH)CH_3), 66.6 (CH(OH)CH_3), 82.5 (C_{Ar}H), 84.5 (C_{Ar}H), 87.0 (C_{Ar}H), 95.0 (Cp*), 100.6 (C_{Ar}), 101.2 (C_{Ar}), 107.9 (C_{Ar}). HRMS-(EI) (*m*/*z*): $[M + H]^+$ calcd for $C_{22}H_{31}ORu.F_6P$, 407.1445; found, 407.1449.

(*E*)-4-(2-(Prop-1-ynyl)cyclohex-1-enyl)but-3-en-2-ol (8-*Dien*) and (*E*)-1-(3-Methoxybut-1-enyl)-2-(prop-1-ynyl)cyclohex-1-ene (10-*Dien*). A 1 M solution of LiHMDS (16.5 mL, 16.5 mmol) in THF was added to a stirred solution of **6**-*Dien-All* (725 mg, 4.11 mmol) in THF (41 mL) at 0 °C. After 20 min of stirring at 0 °C, iodomethane (1.53 mL, 24.7 mmol) was added. After 24 h of stirring while gradually warming to 23 °C, the reaction mixture was poured over saturated aqueous NH_4Cl (80 mL) and extracted with Et_2O (80 mL). The organic extracts were washed with brine (100 mL), dried over $MgSO_4$, concentrated, and purified by flash column chromatography (silica gel). Using a lower concentration of EtOAc as eluent (96:4 hexanes/EtOAc) afforded **10**-*Dien* as a yellow oil (425 mg, 51% yield). Continued elution with a slightly more polar solvent system (92:8 hexanes/EtOAc) afforded **8**-*Dien* as a yellow oil (168 mg, 21% yield). (**8**-*Dien*): IR (ZnSe, neat): 3348 (OH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.31 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH(OH)CH_3), 1.50 (s, 1H, OH), 1.56−1.68 (m, 4H, 4,5-CH_2), 2.03 (s, 3H, C≡CCH_3), 2.16−2.26 (m, 4H, 3,6-CH_2), 4.39−4.47 (m, 1H, C*H*(OH)CH_3), 5.73 (dd, $^3J_{HH}$ = 16 Hz, 7 Hz, 1H, CH=C*H*C(OH)H), 6.93 (d, $^3J_{HH}$ = 16 Hz, 1H, C*H*=CHC(OH)H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 4.8 (C≡CCH_3), 22.3 (CH_2), 22.5 (CH_2), 23.6 (CH_2), 25.2 (CH_2), 31.4 ($CHCH_3$), 69.6 (C(OH)H), 79.8 (C≡C), 91.1 (C≡C), 120.9 (C=C), 130.5 (CH=CH), 132.4 (CH=CH), 138.1 (C=C). HRMS-(EI) (*m*/*z*): $[M + H]^+$ calcd for $C_{13}H_{18}O$, 190.1352; found, 190.1349. (**10**-*Dien*). ^1H NMR (500 MHz, $CDCl_3$): δ 1.27 (d, $^3J_{HH}$ = 6 Hz, 3H, CH(OCH_3)CH_3), 1.56−1.67 (m, 4H, 4,5-CH_2), 2.03 (s, 3H, C≡CCH_3), 2.18−2.25 (m, 4H, 3,6-CH_2), 3.27 (s, 3H, OCH_3), 3.83 (dq, $^3J_{HH}$ = 8 Hz, 6 Hz, 1H, C*H*(OCH_3)CH_3), 5.54 (dd, $^3J_{HH}$ = 16 Hz, 8 Hz, 1H, CH=C*H*C(OCH_3)H), 6.88 (d, $^3J_{HH}$ = 16 Hz, 1H, C*H*=CHC(OCH_3)H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 4.8 (C≡CCH_3), 21.9 (CH_2), 22.3 (CH_2), 22.6 (CH_2), 25.2 (CH_2), 31.4 ($CHCH_3$), 56.1 (OCH_3), 78.7 (*C*(OCH_3)H), 79.9 (C≡C), 90.9 (C≡C), 120.6 (C=C), 130.4 (CH=CH), 132.3 (CH=CH), 138.2 (C=C). HRMS-(EI) (*m*/*z*): $[M + H]^+$ calcd for $C_{14}H_{20}O$, 204.1509; found, 204.1506.

4-(2-(Prop-1-ynyl)cyclohex-1-enyl)but-3-yn-2-ol (8-*Ene*). Anhydrous K_2CO_3 (300 mg, 2.17 mmol) was added to a stirred solution of **12**-*Ene* (80 mg, 0.325 mmol) in THF/MeOH (4 mL, 1/1) at 23 °C. After it was stirred at 23 °C for 3 h, the reaction mixture was diluted with water (10 mL) and extracted with Et_2O (15 mL). The organic extract was washed with brine (10 mL), dried over $MgSO_4$, and concentrated to give the desilylated product as a yellow oil (48 mg, 85% yield). A 1 M solution of LHMDS (1.4 mL, 1.38 mmol) in THF was added to a stirred solution of the resulting product in THF (3 mL) at 0 °C. After the mixture was stirred at 0 °C for 20 min, iodomethane (0.103 mL, 1.65 mmol) was added. After it was stirred for 4 h while being slowly warmed to 23 °C, the reaction mixture was poured over saturated aqueous NH_4Cl (10 mL) and extracted with Et_2O (10 mL). The organic extracts were washed with brine (10 mL),

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dried over $MgSO_4$, concentrated, and purified by flash column chromatography (silica gel, 95/5 hexanes/EtOAc) to afford **8**-*Ene* as a yellow oil (35 mg, 63% yield). IR (ZnSe, thin film): 3348 (OH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.50 (d, $^3J_{HH}$ = 6 Hz, 3H, $CH(OH)CH_3$), 1.55−1.63 (m, 4H, 4,5-CH_2), 1.79 (d, $^3J_{HH}$ = 5.5 Hz, 1H, OH), 2.02 (s, 3H, $C{\equiv}CCH_3$), 2.15−2.22 (m, 4H, 3,6-CH_2), 4.71 (app pentet, $^3J_{HH}$ = 6 Hz, 1H, $CH(OH)CH_3$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 4.7 ($C{\equiv}CCH_3$), 22.0 (2 × CH_2), 24.7 (CH_2), 29.9 (CH_2), 30.5 ($CH(OH)CH_3$), 59.1 ($CH(OH)CH_3$), 80.5 (C≡C), 85.1 (C≡C), 90.1 (C≡C), 94.1 (C≡C), 124.1 (C═C), 127.5 (C═C). HRMS-(EI) (m/z): $[M + H]^+$ calcd for $C_{13}H_{16}O.Na$, 211.1093; found, 211.1097.

6-(1-Hydroxyethyl)-7-methyltetralin (8-*Aryl*). $NaBH_4$ (130 mg, 3.43 mmol) was added to a stirred solution of 6-acetyl-7-methyltetralin (215 mg, 1.14 mmol) in THF/MeOH (12 mL, 1/1) at 23 °C. After it was stirred for 30 min at 23 °C, the reaction mixture was poured over acetone (5 mL), concentrated, diluted with H_2O (10 mL), and extracted with Et_2O (10 mL). The organic extracts were washed with brine (10 mL), dried over Na_2SO_4, and concentrated to afford **8**-*Aryl* as a pale yellow oil (210 mg, 97% yield). IR (ZnSe, neat): 3332 (OH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.47 (d, $^3J_{HH}$ = 6 Hz, 3H, $CH(OH)CH_3$), 1.69 (s, 1H, OH), 1.74−1.83 (m, 4H, 2,3-CH_2), 2.29 (s, 3H, $ArCH_3$), 2.69−2.79 (m, 4H, 1,4-CH_2), 5.08 (q, $^3J_{HH}$ = 6 Hz, 1H, $CH(OH)CH_3$), 6.86 (s, 1H, ArH), 7.21 (s, 1H, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 18.5 ($ArCH_3$), 23.4 (CH_2), 23.5 (CH_2), 24.1 ($CH(OH)CH_3$), 29.0 (CH_2), 29.2 (CH_2), 66.8 ($CH(OH)CH_3$), 125.2 ($C_{Ar}H$), 131.1 ($C_{Ar}H$), 131.4 (C_{Ar}), 135.1 (C_{Ar}), 136.1 (C_{Ar}), 141.2 (C_{Ar}). HRMS-(EI) (m/z): $[M + H]^+$ calcd for $C_{13}H_{18}O.Na$, 213.1250; found, 213.1251.

(η^5-Pentamethylcyclopentadienyl)(η^6-6-(1-hydroxyethyl)-7-methyltetralinyl)ruthenium(II) Hexafluorophosphate (8-*Cp).** After 19 h at 23 °C, the NMR-scale reaction mixture of **8**-*Dien* with **1**-*Cp** was concentrated and purified by flash column chromatography (silica gel, 95/5 CH_2Cl_2/acetone) followed by crystallization (CH_2Cl_2/Et_2O) to afford both **8**-*Cp**-*maj* and **8**-*Cp**-*min* (11.6 mg, 63% combined yield). **8**-*Cp**-*maj* was produced as a colorless solid, while **8**-*Cp**-*min* recrystallized as light brown plates. Data for **8**-*Cp**-*maj* are as follows. Mp: 274−276 °C dec. IR (ZnSe, thin film): 3579 (OH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.48 (d, $^3J_{HH}$ = 6.5 Hz, 3H, $CH(OH)CH_3$), 1.55−1.65 (m, 1H, 2/3-CH_{syn}), 1.81 (s, 15H, Cp*), 1.72−1.87 (m, 3H, 2,3-CH_2), 2.08 (s, 3H, $ArCH_3$), 2.33−2.41 (m, 2H, 1,4-CH_{syn}), 2.66−2.80 (m, 2H, 1,4-CH_{anti}), 2.82 (d, $^3J_{HH}$ = 5.5 Hz, 1H, OH), 4.75 (dq, $^3J_{HH}$ = 6.5 Hz, 5.5 Hz, 1H, $CH(OH)CH_3$), 5.45 (s, 1H, ArH), 5.87 (s, 1H, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 9.8 ($CpCH_3$), 15.7 ($ArCH_3$), 21.8 (CH_2), 21.9 (CH_2), 25.2 ($CH(OH)CH_3$), 25.6 (CH_2), 25.7 (CH_2), 63.7 ($CH(OH)CH_3$), 83.1 ($C_{Ar}H$), 88.7 ($C_{Ar}H$), 94.2 (Cp*), 95.6 (C_{Ar}), 100.5 (C_{Ar}), 101.1 (C_{Ar}), 106.5 (C_{Ar}). HRMS-(EI) (m/z): $[M + H]^+$ calcd for $C_{23}H_{33}ORu.F_6P$, 421.1602; found, 421.1606. Data for **8**-*Cp**-*min* are as follows. Mp: 268−270 °C dec. IR (ZnSe, thin film): 3559 (OH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.56 (d, $^3J_{HH}$ = 6.5 Hz, 3H, $CH(OH)CH_3$), 1.81 (s, 15H, Cp*), 1.64−1.84 (m, 4H, 2,3-CH_2), 2.27 (s, 3H, $ArCH_3$), 2.33−2.41 (m, 2H, 1,4-CH_{syn}), 2.64 (d, $^3J_{HH}$ = 6.5 Hz, 1H, OH), 2.68−2.80 (m, 2H, 1,4-CH_{anti}), 4.68 (pentet, $^3J_{HH}$ = 6.5 Hz, 1H, $CH(OH)CH_3$), 5.39 (s, 1H, ArH), 5.58 (s,1H, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 10.0 ($CpCH_3$), 16.3 ($ArCH_3$), 21.76 (CH_2), 21.78 (CH_2), 22.2 ($CH(OH)CH_3$), 25.5 (CH_2), 25.7 (CH_2), 66.8 ($CH(OH)CH_3$), 85.2 ($C_{Ar}H$), 90.1 ($C_{Ar}H$), 94.0 (Cp*), 98.8 (C_{Ar}), 100.8 (C_{Ar}), 101.4 (C_{Ar}), 103.6 (C_{Ar}). HRMS-(EI) (m/z): $[M + H]^+$ calcd for $C_{23}H_{33}ORu.F_6P$, 421.1602; found, 421.1607.

(*E*)-1-(3-Ethoxybut-1-enyl)-2-(prop-1-ynyl)cyclohex-1-ene (9-*Dien*). Triethylsilyltrifluoromethanesulfonate (0.41 mL, 1.812 mmol) was added to a stirred solution of **6**-*Dien-All* (106 mg, 0.604 mmol, 0.10 M) and imidazole (123 mg, 1.812 mmol, 0.30 M) in THF (6 mL) at 23 °C. After 10 min of stirring at 23 °C, the reaction mixture was quenched with saturated aqueous NH_4Cl (12 mL) and extracted with Et_2O (12 mL). The organic extracts were washed with saturated NH_4Cl (2 × 12 mL), dried over $MgSO_4$, concentrated, and purified by flash column chromatography (alumina, hexanes) to afford a clear oil. A 1 M solution of LHMDS (0.56 mL, 0.56 mmol) in THF was added to a stirred solution of the resulting product in THF (2 mL) at 0 °C. After 20 min of stirring at 0 °C, iodomethane (0.058 mL, 0.93 mmol) was added. After 16 h of stirring with gradual warming to 23 °C, the reaction mixture was poured over saturated aqueous NH_4Cl (4 mL) and extracted with Et_2O (4 mL). The organic extracts were washed with brine (4 mL), dried over $MgSO_4$, concentrated, and purified by reverse-phase column chromatography (C_{18}-bonded silica gel, 9/1 MeOH/H_2O) to afford **9**-*Dien* as a clear oil (21 mg, 16% over two steps). ^1H NMR (400 MHz, $CDCl_3$): δ 1.20 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_2CH_3), 1.28 (d, $^3J_{HH}$ = 7 Hz, 3H, $CH(OEt)CH_3$), 1.56−1.68 (m, 4H, 4,5-CH_2), 2.03 (s, 3H, $C{\equiv}CCH_3$), 2.18−2.26 (m, 4H, 3,6-CH_2), 3.37 (dq, $^2J_{HH}$ = 9 Hz, $^3J_{HH}$ = 7 Hz, 1H, C(H)$H'CH_3$), 3.51 (dq, $^2J_{HH}$ = 9 Hz, $^3J_{HH}$ = 7 Hz, 1H, C(H)H'CH_3), 3.96 (p, $^3J_{HH}$ = 7 Hz, 1H, $CH(OEt)CH_3$), 5.58 (dd, $^3J_{HH}$ = 16 Hz, 7 Hz, 1H, CH═$CHCH(OEt)CH_3$), 6.88 (d, $^3J_{HH}$ = 16 Hz, 1H, CH═CHCH(OEt)-CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 4.8 ($C{\equiv}CCH_3$), 15.6 (CH_2CH_3), 22.2 (CH_2), 22.3 (CH_2), 22.6 (CH_2), 25.2 (CH_2), 31.3 ($CH(OEt)CH_3$), 63.6 (CH_2CH_3), 76.8 ($CH(OEt)CH_3$), 79.9 (C≡C), 90.8 (C≡C), 120.4 (C═C), 131.0 (CH═CH), 131.6 (CH═CH), 138.3 (C═C). HRMS-(EI) (m/z): $[M + H]^+$ calcd for $C_{15}H_{23}O$, 219.1743; found, 219.1742.

(η^5-Pentamethylcyclopentadienyl)(η^6-6-(1-ethoxyethyl)-7-methyltetralinyl)ruthenium(II) Hexafluorophosphate (9-*Cp).** After 3.5 h at 23 °C, the NMR-scale reaction mixture of **9**-*Dien* with **1**-*Cp** was concentrated and purified by flash column chromatography (alumina, CH_2Cl_2) to afford a mixture of **9**-*Cp**-*maj* and **9**-*Cp**-*min* as a colorless solid (14 mg, 63% yield). ^1H NMR (400 MHz, $CDCl_3$): δ 1.22 (t, $^3J_{HH}$ = 7 Hz, 3H, *min*-CH_2CH_3), 1.30 (t, $^3J_{HH}$ = 7 Hz, 3H, *maj*-CH_2CH_3), 1.38 (d, $^3J_{HH}$ = 6 Hz, 3H, *maj*−$CH(OH)CH_3$), 1.48 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *min*−$CH(OH)CH_3$), 1.80 (s, 15H, *maj*-Cp*), 1.81 (s, 15H, *min*-Cp*), 1.56−1.86 (m, 8H, 2,3-CH_2), 2.10 (s, 3H, *maj*-$ArCH_3$), 2.22 (s, 3H, *min*-$ArCH_3$), 2.31−2.46 (m, 4H, 1,4-CH_{syn}), 2.68−2.77 (m, 4H, 1,4-CH_{anti}), 3.45 (dq, $^2J_{HH}$ = 9 Hz, $^3J_{HH}$ = 7 Hz, 2H, C(H)$H'CH_3$), 3.71 (dq, $^2J_{HH}$ = 9 Hz, $^3J_{HH}$ = 7 Hz, 1H, *min*-C(H)H'CH_3), 3.84 (dq, $^2J_{HH}$ = 9 Hz, $^3J_{HH}$ = 7 Hz, 1H, *maj*-C(H)H'CH_3), 4.28 (q, $^3J_{HH}$ = 6.5 Hz, 1H, *min*-$CH(OH)CH_3$), 4.30 (q, $^3J_{HH}$ = 6 Hz, 1H, *maj*-$CH(OH)CH_3$), 5.48 (s, 1H, *min*-ArH), 5.61 (s, 1H, *min*-ArH), 5.67 (s, 2H, *maj*-ArH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 9.8 (*maj*-$CpCH_3$), 10.0 (*min*-$CpCH_3$), 15.65 (*maj*-CH_3), 15.74 (*maj*-CH_3), 16.0 (*min*-CH_3), 16.3 (*min*-CH_3), 17.8 (*min*-CH_3), 20.6 (*maj*-CH_3), 21.8 (1 × *maj*-CH_2, 2 × *min*-CH_2), 21.9 (*maj*-CH_2), 25.4 (*min*-CH_2), 25.6 (*maj*-CH_2), 25.8 (*min*-CH_2), 25.9 (*maj*-CH_2), 63.7 (*maj*-CH_2CH_3), 64.2 (*min*-CH_2CH_3), 70.3 (*maj*-$CH(OH)CH_3$), 73.5 (*min*-$CH(OH)CH_3$), 83.3 (*maj*-$C_{Ar}H$), 85.1 (*min*-$C_{Ar}H$), 89.2 (*maj*-$C_{Ar}H$), 90.1 (*min*-$C_{Ar}H$), 94.0 (*maj*-Cp*), 94.2 (*min*-Cp*), 95.5 (*maj*-C_{Ar}), 98.5 (*min*-C_{Ar}), 100.0 (*maj*-C_{Ar}), 100.8 (*min*-C_{Ar}), 101.7 (*min*-C_{Ar}), 101.8 (*maj*-C_{Ar}), 103.0 (*min*-C_{Ar}), 105.7 (*maj*-C_{Ar}). HRMS-(EI) (m/z): $[M + H]^+$ calcd for $C_{25}H_{37}ORu.F_6P$, 449.1915; found, 449.1927.

(η^5-Pentamethylcyclopentadienyl)(η^6-6-(1-methoxyethyl)-7-methyltetralinyl)ruthenium(II) Hexafluorophosphate (10-*Cp).** Ruthenium complex **1**-*Cp** (34 mg, 0.068 mmol) was added to a solution of **10**-*Dien* (12 mg, 0.058 mmol) in $CDCl_3$ at 23 °C in a glovebox. After 30 min at 23 °C, the reaction mixture was concentrated and purified by repeated PTLC (CH_2Cl_2/acetone mixtures) followed by recrystallization (EtOAc/CH_2Cl_2/hexanes) to afford isolated samples of **10**-*Cp**-*maj* and **10**-*Cp**-*min* as colorless solids. Data for **10**-*Cp**-*maj* are as follow.s Mp: 274−277 °C dec. ^1H NMR (400 MHz, $CDCl_3$): δ 1.39 (d, $^3J_{HH}$ = 6 Hz, 3H, $CH(OMe)CH_3$), 1.80 (s, 15H, Cp*), 1.52−1.88 (m, 4H, 2,3-CH_2), 2.11 (s, 3H, $ArCH_3$), 2.27−2.47 (m, 2H, 1,4-CH_{syn}), 2.66−2.78 (m, 2H, 1,4-CH_{anti}), 3.47 (s, 3H, OCH_3), 4.20 (q, $^3J_{HH}$ = 6 Hz, 1H, $CH(OMe)CH_3$), 5.62 (s, 1H, ArH), 5.68 (s, 1H, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 9.8 (Cp*), 15.7 (CH_3), 19.9 (CH_3), 21.8 (CH_2), 21.9 (CH_2), 25.6 (CH_2), 25.8 (CH_2), 56.0 (OCH_3), 71.9 ($CH(OMe)CH_3$), 83.2 ($C_{Ar}H$), 89.1 ($C_{Ar}H$), 94.1 (Cp*), 95.9 (C_{Ar}), 100.0 (C_{Ar}), 101.7 (C_{Ar}), 105.3 (C_{Ar}). HRMS-(EI) (m/z): $[M + H]^+$ calcd for $C_{24}H_{35}ORu.F_6P$, 441.1726; found, 441.1725. Data for **10**-*Cp**-*min* are as follows. Mp: 196−197 °C dec. ^1H NMR (400 MHz, $CDCl_3$): δ 1.47 (d, $^3J_{HH}$ = 6 Hz, 3H, $CH(OMe)CH_3$), 1.81 (s, 15H,

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Cp*), 1.62−1.87 (m, 4H, 2,3-CH_2), 2.21 (s, 3H, $ArCH_3$), 2.35−2.45 (m, 2H, 1,4-CH_{syn}), 2.68−2.78 (m, 2H, 1,4-CH_{anti}), 3.40 (s, 3H, OCH_3), 4.17 (q, $^3J_{HH}$ = 6 Hz, 1H, C*H*(OMe)CH_3), 5.41 (s, 1H, ArH), 5.63 (s, 1H, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 10.0 (Cp*), 16.4 (CH_3), 17.5 (CH_3), 21.8 (2 × CH_2), 25.4 (CH_2), 25.7 (CH_2), 56.1 (OCH_3), 75.9 (CH(OMe)CH_3), 85.8 ($C_{Ar}H$), 90.1 ($C_{Ar}H$), 94.3 (Cp*), 98.2 (C_{Ar}), 100.9 (C_{Ar}), 101.4 (C_{Ar}), 103.4 (C_{Ar}). HRMS-(EI) (*m*/*z*): [M + H]$^+$ calcd for $C_{24}H_{35}ORu.F_6P$, 441.1726; found, 441.1727.

(η^5-Cyclopentadienyl)(η^6-6-(1-methoxyethyl)-7-methyltetralinyl)ruthenium(II) Hexafluorophosphate (10-*Cp*). After 30 min at 23 °C, the NMR-scale reaction mixture of **10**-*Dien* with **1**-*Cp* was concentrated and purified by flash column chromatography (silica gel, CH_2Cl_2) followed by crystallization (CH_2Cl_2/Et_2O) to afford a mixture of **10**-*Cp-maj* and **10**-*Cp-min* as a colorless solid. **10**-*Cp-maj* and **10**-*Cp-min* were each isolated after repeated flash column chromatography (silica gel). Data for **10**-*Cp-maj* are as follows. Mp: 167−169 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 1.40 (d, $^3J_{HH}$ = 6 Hz, 3H, CH(OMe)CH_3), 1.66−1.91 (m, 4H, 2,3-CH_2), 2.31 (s, 3H, $ArCH_3$), 2.53−2.84 (m, 4H, 1,4-CH), 3.49 (s, 3H, OCH_3), 4.34 (q, $^3J_{HH}$ = 6 Hz, 1H, C*H*(OMe)CH_3), 5.17 (s, 5H, Cp), 6.11 (s, 1H, ArH), 6.17 (s, 1H, ArH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 17.8 (CH_3), 20.7 (CH_3), 22.3 (CH_2), 22.4 (CH_2), 27.7 (CH_2), 28.3 (CH_2), 57.1 (OCH_3), 73.2 (*C*H(OMe)CH_3), 81.4 (Cp), 81.5 ($C_{Ar}H$), 87.8 ($C_{Ar}H$), 98.2 (C_{Ar}), 101.4 (C_{Ar}), 102.7 (C_{Ar}), 106.4 (C_{Ar}). HRMS-(EI) (*m*/*z*): [M + H]$^+$ calcd for $C_{19}H_{25}ORu.F_6P$, 365.0976; found, 365.0977. Data for **10**-*Cp-min* are as follows. Mp: 188−189 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 1.51 (d, $^3J_{HH}$ = 6 Hz, 3H, CH(OMe)CH_3), 1.69−1.89 (m, 4H, 2,3-CH_2), 2.36 (s, 3H, $ArCH_3$), 2.64−2.83 (m, 4H, 1,4-CH), 3.36 (s, 3H, OCH_3), 4.37 (q, $^3J_{HH}$ = 6 Hz, 1H, C*H*(OMe)CH_3), 5.19 (s, 5H, Cp), 6.12 (s, 1H, ArH), 6.14 (s, 1H, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 18.3 (CH_3), 20.7 (CH_3), 22.2 (CH_2), 22.3 (CH_2), 27.8 (CH_2), 28.1 (CH_2), 57.2 (OCH_3), 74.4 (*C*H(OMe)CH_3), 81.5 (Cp), 84.0 ($C_{Ar}H$), 87.7 ($C_{Ar}H$), 100.1 (C_{Ar}), 101.6 (C_{Ar}), 102.8 (C_{Ar}), 106.1 (C_{Ar}). HRMS-(EI) (*m*/*z*): [M + H]$^+$ calcd for $C_{19}H_{25}ORu.F_6P$, 365.0976; found, 365.0979.

(*E*)-Ethyl 3-(2-((Trimethylsilyl)ethynyl)cyclohex-1-enyl)-acrylate (11-*Dien-Precursor*-1). Ethyl (triphenylphosphoranylidene)acetate (1.87 g, 5.37 mmol) and **7** (1.00 g, 4.85 mmol) were refluxed in benzene (4.8 mL) for 2 h, concentrated, and purified by flash column chromatography (silica gel, 95/5 hexanes/EtOAc) to afford **11**-*Dien-Precursor*-1 as a yellow solid (1.22 g, 91% yield). Mp: 44−46 °C. IR (ZnSe, thin film): 2139 (C≡C), 1710 (C═O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.24 (s, 9H, TMS), 1.31 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH_2CH_3), 1.59−1.71 (m, 4H, 4,5-CH_2), 2.20−2.26 (m, 2H, 6-CH_2), 2.30−2.36 (m, 2H, 3-CH_2), 4.22 (q, $^3J_{HH}$ = 7.0 Hz, 2H, CH_2CH_3), 5.88 (d, $^3J_{HH}$ = 16.1 Hz, 1H, CH═*C*HCO$_2$Et), 8.06 (d, $^3J_{HH}$ = 16.1 Hz, 1H, *C*H═CHCO$_2$Et). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 0.1 (TMS), 14.5 (CH_2CH_3), 21.9 (CH_2), 22.0 (CH_2), 25.0 (CH_2), 31.3 (CH_2), 60.4 (CH_2CH_3), 102.3 (C≡C), 104.3 (C≡C), 117.7 (CH═CH), 127.8 (C═C), 139.9 (C═C), 144.2 (CH═CH), 167.6 (CO_2Et). HRMS-(EI) (*m*/*z*): [M + H]$^+$ calcd for $C_{16}H_{24}O_2Si$, 276.1540; found, 276.1543.

(*E*)-3-(2-((Trimethylsilyl)ethynyl)cyclohex-1-en-1-yl)prop-2-en-1-ol (11-*Dien-Precursor*-2). Lithium aluminum hydride (103 mg, 2.71 mmol) was added to a stirred solution of **11**-*Dien-Precursor*-1 (250 mg, 0.904 mmol) in Et_2O (9 mL) at 0 °C. After it was stirred at 0 °C for 10 min, the reaction mixture was quenched by sequential addition of H_2O (0.40 mL), 1.3 M aqueous NaOH (0.80 mL), and H_2O (1.2 mL), filtered through anhydrous K_2CO_3, and concentrated to afford **11**-*Dien-Precursor*-2 as a colorless oil (209 mg, 99% yield). IR (ZnSe, neat): 3332 (OH), 2134 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.21 (s, 9H, TMS), 1.35 (bs, 1H, OH), 1.56−1.70 (m, 4H, 4,5-CH_2), 2.20−2.30 (m, 4H, 3,6-CH_2), 4.25 (d, $^3J_{HH}$ = 6.0 Hz, 2H, CH_2OH), 5.90 (dt, $^3J_{HH}$ = 15.6 Hz, $^3J_{HH}$ = 6.0 Hz, 1H, CH═*C*HCH$_2$), 7.00 (d, $^3J_{HH}$ = 15.6 Hz, 1H, *C*H═CHCH$_2$). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 0.3 (TMS), 22.1 (CH_2), 22.4 (CH_2), 25.3 (CH_2), 30.8 (CH_2), 64.3 (CH_2OH), 99.5 (C≡C), 105.3 (C≡C), 120.2 (C═C), 128.2 (CH═CH), 132.0 (CH═CH), 140.9 (C═C). HRMS-(EI) (*m*/*z*): [M + H]$^+$ calcd for $C_{14}H_{22}OSi.Na$, 257.1332; found, 257.1334.

(*E*)-4-Methyl-1-(2-(prop-1-ynyl)cyclohex-1-enyl)pent-1-en-3-ol (11-*Dien*). 2-Iodoxybenzoic acid[21] (373 mg, 1.33 mmol, 0.21 M) was added to a solution of **11**-*Dien-Precursor*-2 (208 mg, 0.887 mmol) in EtOAc (6.5 mL), refluxed for 6 h, cooled to 23 °C, filtered, and concentrated to afford a yellow oil (215 mg, 0.925 mmol). A 2 M solution of *i*-PrMgCl (0.93 mL, 1.85 mmol) in THF was added to a stirred solution of the resulting product in THF (10 mL) at 0 °C. After 20 min of stirring at 0 °C, the reaction mixture was quenched with MeOH (3 mL), diluted with saturated aqueous NH_4Cl (15 mL), and extracted with Et_2O (20 mL). The organic extracts were washed with water (2 × 10 mL) and brine (10 mL), dried over $MgSO_4$, and concentrated to afford a yellow oil. Anhydrous K_2CO_3 (112 mg, 0.814 mmol) was added to a stirred solution of the resulting product in MeOH/THF (3 mL, 1/1) at 23 °C. After 4 h of stirring at 23 °C, the reaction mixture was filtered through a fritted funnel, concentrated, diluted with aqueous 1 M HCl (5 mL), and extracted with Et_2O (5 mL). The organic extracts were washed with 1 M HCl (5 mL), water (5 mL), and brine (5 mL), dried over $MgSO_4$, concentrated, and purified by flash column chromatography (silica gel, 96/4 hexanes/EtOAc) to afford the terminal alkyne as a yellow oil (44 mg, 0.215 mmol). A 1 M solution of LHMDS (0.70 mL, 0.698 mmol) in THF was added to a stirred solution of the resulting product in THF (2 mL) at 0 °C. After 20 min of stirring at 0 °C, iodomethane (0.067 mL, 1.075 mmol) was added. After 1 h of stirring with gradual warming to 23 °C, the reaction mixture was poured over saturated aqueous NH_4Cl (4 mL) and extracted with Et_2O (4 mL). The organic extracts were washed with brine (4 mL), dried over $MgSO_4$, concentrated, and purified by flash column chromatography (silica gel, 96/4 hexanes/EtOAc) to afford **11**-*Dien* as a clear oil (22 mg, 11% yield over four steps). IR (ZnSe, neat): 3332 (OH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.90 (d, $^3J_{HH}$ = 7 Hz, 3H, CH(CH_3)CH_3), 0.96 (d, $^3J_{HH}$ = 7 Hz, 3H, CH(CH_3)CH_3), 1.46 (m, 1H, OH), 1.56−1.69 (m, 4H, 4,5-CH_2), 1.76 (octet, $^3J_{HH}$ = 7 Hz, 1H, C*H*(CH_3)$_2$), 2.03 (s, 3H, C≡CCH_3), 2.17−2.27 (m, 4H, 3,6-CH_2), 3.94 (t, $^3J_{HH}$ = 7 Hz, 1H, C*H*(OH)CH), 5.70 (dd, $^3J_{HH}$ = 16 Hz, 7.5 Hz, 1H, CH═*C*HCH(OH)CH), 6.93 (d, $^3J_{HH}$ = 16 Hz, 1H, C*H*═CHCH(OH)-CH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 4.8 (C≡*C*CH$_3$), 18.3 (CH(*C*H$_3$)CH$_3$), 18.6 (CH(*C*H$_3$)CH$_3$), 22.3 (CH_2), 22.5 (CH_2), 25.3 (CH_2), 31.4 (CH_2), 34.2 (CH(CH_3)CH_3), 78.7 (*C*H(OH)CH), 79.8 (C≡*C*), 91.0 (C≡*C*), 120.7 (C═*C*), 129.8 (CH═*C*H), 132.2 (*C*H═CH), 138.3 (*C*═C). HRMS-(EI) (*m*/*z*): [M + H]$^+$ calcd for $C_{14}H_{20}O.Na$, 241.1563; found, 241.1567.

(*E*)-4-(2-((Trimethylsilyl)ethynyl)cyclohex-1-enyl)but-3-en-2-one (12-*Dien-Precursor*). 1-(Triphenylphosphoranylidene)-2-propanone (640 mg, 2.01 mmol) and **7** (398 mg, 1.93 mmol) were refluxed in toluene (1 mL) for 1.5 h, concentrated, and purified by flash column chromatography (silica gel, 93/7 hexanes/EtOAc) to afford **12**-*Dien-Precursor* as a yellow solid (307 mg, 65% yield). Mp: 45−50 °C. IR (KBr, neat): 2137 (C≡C), 1691 (C═O) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 0.23 (s, 9H, TMS), 1.59−1.70 (m, 4H, 4,5-CH_2), 2.20−2.24 (m, 2H, 6-CH_2), 2.30−2.35 (m, 2H, 3-CH_2), 2.31 (s, 3H, C(O)CH_3), 6.10 (d, $^3J_{HH}$ = 16 Hz, 1H, CH═*C*HC(O)CH_3), 7.91 (d, $^3J_{HH}$ = 16 Hz, 1H, *C*H═CHC(O)CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 0.1 (TMS), 21.8 (CH_2), 21.9 (CH_2), 24.9 (CH_2), 26.3 (CH_3), 31.3 (CH_2), 102.8 (C≡*C*), 104.1 (C≡*C*), 127.1 (CH═*C*HC(O)CH_3), 128.7 (1-C), 140.2 (2-C), 143.7 (*C*H═CHC(O)-CH_3), 199.5 (*C*(O)CH_3). HRMS-(EI) (*m*/*z*): [M + H]$^+$ calcd for $C_{15}H_{22}OSi$, 246.1434; found, 246.1434.

(*E*)-4-(2-((Trimethylsilyl)ethynyl)cyclohex-1-enyl)but-3-en-2-ol (12-*Dien*). $NaBH_4$ (374 mg, 9.89 mmol) was added to a stirred solution of **12**-*Dien-Precursor* (812 mg, 3.30 mmol) in MeOH/THF (66 mL, 1/1) at 23 °C. After 10 min of stirring at 23 °C, the reaction mixture was diluted with saturated aqueous NH_4Cl (100 mL) and extracted with Et_2O (2 × 100 mL). The organic extracts were washed with brine (200 mL), dried over $MgSO_4$, and concentrated to afford **12**-*Dien* as a pale yellow oil (775 mg, 95% yield). IR (NaCl, neat): 3345 (OH), 2135 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.21 (s, 9H, TMS), 1.32 (d, $^3J_{HH}$ = 7 Hz, 3H, CH_3), 1.50−1.68 (m, 5H, 4,5-

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CH_2, OH), 2.19−2.28 (m, 4H, 3,6-CH_2), 4.41 (p, $^3J_{HH}$ = 7 Hz, 1H, C(*H*)OH), 5.79 (dd, $^3J_{HH}$ = 16 Hz, 7 Hz, 1H, CH═*CH*C(H)OH), 6.96 (d, $^3J_{HH}$ = 16 Hz, 1H, *CH*═CHC(H)OH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 0.3 (TMS), 22.1 (CH_2), 22.4 (CH_2), 23.4 (CH_2), 25.3 (CH_2), 30.7 (CH_3), 69.4 (CH(OH)), 99.5 (C≡C), 105.3 (C≡C), 120.1 (C═C), 130.2 (CH═CH), 133.3 (CH═CH), 141.0 (C═C). HRMS-(EI) (*m*/*z*): $[M + H]^+$ calcd for $C_{15}H_{24}OSi$, 248.1591; found, 248.1589.

4-(2-((Trimethylsilyl)ethynyl)cyclohex-1-enyl)but-3-yn-2-ol (12-*Ene*). A 1 M solution of LHMDS (9.19 mL, 9.19 mmol) in THF was added to a stirred solution of **13**-*Ene* (620 mg, 3.06 mmol) in THF (31 mL) at 0 °C. After the mixture was stirred at 0 °C for 30 min, acetaldehyde (0.86 mL, 15.32 mmol) was added. After it was stirred at 0 °C for 30 min, the reaction mixture was poured over saturated aqueous NH_4Cl (60 mL) and extracted with Et_2O (60 mL). The organic extracts were washed with brine (60 mL), dried over $MgSO_4$, concentrated, and purified by flash column chromatography (silica gel, 95/5 hexanes/EtOAc) to afford **12**-*Ene* as a yellow oil (573 mg, 76% yield). IR (NaCl, neat): 3364 (OH), 2140 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.20 (s, 9H, TMS), 1.50 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH(OH)*CH*$_3$), 1.58−1.61 (m, 4H, 4,5-CH_2), 1.82 (d, $^3J_{HH}$ = 6.5 Hz, 1H, OH), 2.17−2.24 (m, 4H, 3,6-CH_2), 4.70 (p, $^3J_{HH}$ = 6.5 Hz, 1H, *CH*(OH)CH_3). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 0.2 (TMS), 21.8 (2 × CH_2), 24.6 (CH_2), 29.9 (CH_2), 30.0 (CH(OH)*CH*$_3$), 59.0 (*CH*(OH)CH_3), 84.7 (C≡C), 95.2 (C≡C), 98.2 (C≡C), 105.6 (C≡C), 126.7 (C═C), 127.0 (C═C). HRMS-(EI) (*m*/*z*): $[M + H]^+$ calcd for $C_{15}H_{22}OSi$, 246.1434; found, 246.1432.

(η⁵-Pentamethylcyclopentadienyl)(η⁶-6-(1-hydroxyethyl)-7-trimethylsilyltetralinyl)ruthenium(II) Hexafluorophosphate (12-*Cp) and (η⁵-Pentamethylcyclopentadienyl)(η⁶-6-(1-trimethylsiloxyethyl)tetralinyl)ruthenium(II) Hexafluorophosphate (14-*Cp**-*min*).** Ruthenium complex **1**-*Cp** (50 mg, 0.099 mmol) was added to a solution of 12-*Ene* (29 mg, 0.119 mmol) in THF/acetone (1/1, 2 mL) at 23 °C in a glovebox. After 30 min at 23 °C, the reaction mixture was concentrated and purified by repeated flash column chromatography (silica gel, CH_2Cl_2/acetone mixtures) followed by crystallization (CH_2Cl_2/Et_2O) of separated fractions to afford isolated samples of **12**-*Cp**-*maj* and isomerized **14**-*Cp**-*min* as colorless solids. **12**-*Cp**-*min* was obtained as a mixture with **14**-*Cp**-*min*. Only a small quantity of **14**-*Cp**-*maj* was isolated, and spectroscopic assignments were verified by a separate arene binding reaction (*vide infra*). Data for **12**-*Cp**-*maj* are as follows. Mp: 205−207 °C dec. IR (ZnSe, thin film): 3572 (OH) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.41 (s, 9H, TMS), 1.56 (d, $^3J_{HH}$ = 6 Hz, 3H, CH(OH)*CH*$_3$), 1.60−1.69 (m, 1H, 2/3-CH_{syn}), 1.85 (s, 15H, Cp*), 1.75−1.93 (m, 3H, 2,3-CH_{anti}, 2/3-CH_{syn}), 2.31 (dt, J_{HH} = 17 Hz, 5.5 Hz, 1H, 1/4-CH_{syn}), 2.48 (dt, J_{HH} = 17 Hz, 6 Hz, 1H, 1/4-CH_{syn}), 2.64−2.73 (m, 1H, 1/4-CH_{anti}), 2.85 (dt, J_{HH} = 17 Hz, 6 Hz, 1H, 1/4-CH_{anti}), 2.96 (d, $^3J_{HH}$ = 6 Hz, 1H, OH), 4.69 (p, $^3J_{HH}$ = 6 Hz, 1H, *CH*(OH)CH_3), 5.28 (s, 1H, ArH), 6.00 (s, 1H, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 1.3 (TMS), 10.7 (Cp*CH*$_3$), 21.8 (CH_2), 21.9 (CH_2), 25.1, 26.2, 27.1 (2 × CH_2, CH(OH)*CH*$_3$), 66.3 (*CH*(OH)CH_3), 84.1 ($C_{Ar}H$), 88.9 ($C_{Ar}H$), 92.8 (C_{Ar}), 94.9 (*Cp*CH_3), 100.7 (C_{Ar}), 102.1 (C_{Ar}), 112.5 (C_{Ar}). HRMS-(EI) (*m*/*z*): $[M+H]^+$ calcd for $C_{25}H_{39}ORuSi.F_6P$, 485.1808; found, 485.1807. Data for **12**-*Cp**-*min* are as follows. ^1H NMR (300 MHz, $CDCl_3$): δ 0.40 (s, 9H, TMS), 1.57 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH(OH)*CH*$_3$), 1.60−1.69 (m, 1H, 2/3-CH_{syn}), 1.83 (s, 15H, Cp*), 1.75−1.93 (m, 3H, 2,3-CH_{anti}, 2/3-CH_{syn}), 2.27−2.49 (m, 4H, 1,4-CH_{syn}), 2.66 (d, $^3J_{HH}$ = 6.5 Hz, 1H, OH), 2.63−2.87 (m, 4H, 1,4-CH_{anti}), 4.59 (p, $^3J_{HH}$ = 6.5 Hz, 1H, *CH*(OH)CH_3), 5.42 (s, 1H, ArH), 5.65 (s, 1H, ArH). Data for **14**-*Cp**-*min* are as follows. Mp: 245 °C dec (brown onset). ^1H NMR (300 MHz, $CDCl_3$): δ 0.22 (s, 9H, TMS), 1.51 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH(OTMS)*CH*$_3$), 1.86 (s, 15H, Cp*), 1.63−1.91 (m, 4H, 2,3-CH_2), 2.36−2.52 (m, 2H, 1,4-CH_{syn}), 2.69−2.84 (m, 2H, 1,4-CH_{anti}), 4.69 (q, $^3J_{HH}$ = 6.5 Hz, 1H, *CH*(OTMS)CH_3), 5.55 (d, $^3J_{HH}$ = 6.5 Hz, 1H, ArH), 5.68 (s, 1H, 5-ArH), 5.81 (d, $^3J_{HH}$ = 6.5 Hz, 1H, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 1.1 (TMS), 10.4 (Cp*CH*$_3$), 21.7 (CH_2), 21.8 (CH_2), 25.9, 26.3, 27.0 (2 × CH_2, CH(OTMS)*CH*$_3$), 67.7 (CH(OTMS)CH_3), 82.8 ($C_{Ar}H$), 83.9 ($C_{Ar}H$), 86.8 ($C_{Ar}H$), 94.7 (*Cp*CH_3), 100.9 (C_{Ar}), 101.6 (C_{Ar}), 108.8 (C_{Ar}). HRMS-(EI) (*m*/*z*): $[M + H]^+$ calcd for $C_{25}H_{38}ORuSi.F_6P$, 484.1730; found, 484.1734.

(η⁵-1-Trifluoromethyl-2,3,4,5-tetramethylcyclopentadienyl)(η⁶-6-(1-hydroxyethyl)-7-trimethylsilyltetralinyl)ruthenium(II) Hexafluorophosphate (12-*Cp*‡). Ruthenium complex **1**-*Cp*‡ (100 mg, 180 μmol) was added to a solution of **12**-*Ene* (50 mg, 200 μmol) in acetone/THF (10 mL, 1/1) in the glovebox. The mixture was allowed to react for 60 min and then concentrated under vacuum. The residue was dissolved in a minimal amount of methylene chloride, and then the ruthenium complexes were precipitated by addition of Et_2O. The precipitate was collected on a fine frit and washed with Et_2O. The mixture of **12**-*Cp*‡ was then purified by flash column chromatography (silica gel, 0−2% gradient acetone/CH_2Cl_2) to give **12**-*Cp*‡-*maj* (14.7 mg, 13% yield), and **12**-*Cp*‡-*min* (15.9 mg, 14% yield) as white solids. Data for **12**-*Cp*‡-*maj* are as follows. ^1H NMR (500 MHz, $CDCl_3$): δ 0.43 (s, 9H, TMS), 1.54 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH(OH)*CH*$_3$), 1.65−1.79 (m, 4H, 2,3-CH_2), 1.91 (s, 3H, Cp‡*CH*$_3$), 1.94 (bs, 3H, Cp‡*CH*$_3$), 1.96 (s, 3H, Cp‡*CH*$_3$), 2.05 (bs, 3H, Cp‡*CH*$_3$), 2.39−2.52 (m, 2H, 1,4-$CH_{2,syn}$), 2.69−2.75 (m, 1H, 1,4-$CH_{2,anti}$), 2.84 (dt, $^2J_{HH}$ = 17.9 Hz, $^3J_{HH}$ = 5.6 Hz, 1H, 1,4-$CH_{2,anti}$), 3.10 (d, $^3J_{HH}$ = 6.5 Hz, 1H, O*H*), 4.69 (p, $^3J_{HH}$ = 6.5 Hz, 1H), 5.55 (s, 1H, ArH), 6.11 (s, 1H, ArH). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 0.69 (TMS), 10.0 (Cp‡CH_3), 10.1 (Cp‡CH_3), 10.4 (Cp‡CH_3), 11.4 (Cp‡CH_3), 21.2 (CH_2), 21.5 (CH_2), 25.3 (CH_2), 26.5 (CH_2), 26.7 (CH_2), 65.7 (*CH*(OH)), 84.6 (q, $^1J_{CF}$ = 270 Hz, $C_{Cp}CF_3$), 84.8 ($C_{Ar}H$), 89.3 ($C_{Ar}H$), 92.6 ($C_{Cp}CH_3$), 94.2 ($C_{Cp}CH_3$), 95.4 (C_{Ar}TMS), 97.4 ($C_{Cp}CH_3$), 98.3 ($C_{Cp}CH_3$), 103.4 ($C_{Ar}CH_2$), 104.32 ($C_{Ar}CH_2$), 114.2 (C_{Ar}CH(OH)), 125.3 (q, $^1J_{CF}$ = 270 Hz, CF_3). ^{19}F NMR (470 MHz, $CDCl_3$): δ −54.40 (CF_3), −72.2 (d, $^1J_{PF}$ = 712.8 Hz, PF_6). HRMS-(ESI) (*m*/*z*): $[M + H]^+$ calcd for $C_{25}H_{36}F_3ORuSi.F_6P$, 539.1538; found, 539.1525. Data for **12**-*Cp*‡-*min* are as follows. ^1H NMR (500 MHz, $CDCl_3$): δ 0.38 (s, 9H, TMS), 1.55 (d, $^3J_{HH}$ = 6.4 Hz, CH(OH)*CH*$_3$), 1.71 (m, 2H, 2,3-CH_2), 1.82 (m, 2H, 2,3-CH_2), 1.87 (s, 3H, Cp‡*CH*$_3$), 1.88 (s, 3H, Cp‡*CH*$_3$), 1.93 (bs, 3H, Cp‡*CH*$_3$), 1.98 (bs, 3H, Cp‡*CH*$_3$), 2.38−2.50 (m, 2H, 1,4-CH_{2syn}), 2.73 (dt, $^2J_{HH}$ = 17.4 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, 1,4-$CH_{2,anti}$), 2.84 (dt, $^2J_{HH}$ = 17.7 Hz, $^3J_{HH}$ = 6.5 Hz, 1H, 1,4-$CH_{2,anti}$), 3.15 (bs, 1H, OH), 4.58 (q, $^3J_{HH}$ = 6.4 Hz, 1H, *CH*(OH)CH_3), 5.67 (s, 1H, ArH), 5.83 (s, 1H, ArH). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 1.5 (TMS), 10.1 (Cp‡CH_3), 10.3 (Cp‡CH_3), 10.4 (Cp‡CH_3), 11.1 (Cp‡CH_3), 21.4 (CH_2), 21.5 (CH_2), 21.9 (CH(OH)CH_3), 25.4 (CH_2), 26.2 (CH_2), 66.9 (CH(OH)CH_3), 84.3 (q, 36.5 Hz, $C_{Cp}CF_3$), 86.1 ($C_{Ar}H$), 91.8 ($C_{Ar}H$), 92.6 ($C_{Cp}CH_3$), 93.8 ($C_{Cp}CH_3$), 96.6 (C_{Ar}TMS), 96.7 ($C_{Cp}CH_3$), 98.9 ($C_{Cp}CH_3$), 103.7 ($C_{Ar}CH_2$), 104.6 ($C_{Ar}CH_2$), 110.6 ($C_{Ar}CH_2$), 125.1 (q, $^1J_{CF}$ = 272.3 Hz, CF_3). ^{19}F NMR (470 MHz, $CDCl_3$): δ −54.6 (CF_3), −72.2 (d, $^1J_{PF}$ = 712.2 Hz, PF_6) HRMS-(ESI) (*m*/*z*): $[M + H]^+$ calcd for $C_{25}H_{36}F_3ORuSi.F_6P$, 539.1538; found, 539.1537.

(η⁵-Cyclopentadienyl)(η⁶-6-(1-hydroxyethyl)-7-trimethylsilyltetralinyl)ruthenium(II) Hexafluorophosphate (12-*Cp*). Ruthenium complex **1**-*Cp* (50 mg, 0.114 mmol) was added to a solution of **12**-*Ene* (53 mg, 0.215 mmol) and γ-terpinene (0.070 mL, 0.437 mmol) in acetone-d_6 (11 mL) at 23 °C in a glovebox. After 16 h at 23 °C, the reaction mixture was concentrated and purified by repeated flash column chromatography (silica gel, acetone/CH_2Cl_2 solvent mixtures) followed by crystallization (CH_2Cl_2/EtOAc/hexanes) to afford a mixture of diastereomers **12**-*Cp*-*dias*^{1} and **12**-*Cp*-*dias*^{2} as a colorless solid. Data for **12**-*Cp* (mixture) are as follows. ^1H NMR (300 MHz, $CDCl_3$): δ 0.42 (s, 18H, TMS), 1.51 (d, $^3J_{HH}$ = 6 Hz, 3H, *dias*^{1}-CH(OH)*CH*$_3$), 1.56 (d, $^3J_{HH}$ = 6 Hz, 3H, *dias*^{2}-CH(OH)*CH*$_3$), 1.68−1.92 (m, 8H, 2,3-CH_2), 2.57−2.93 (m, 9H, 1,4-CH_2, *dias*^{2}-OH), 3.11 (d, $^3J_{HH}$ = 6 Hz, *dias*^{1}-OH), 4.66 (p, $^3J_{HH}$ = 6 Hz, 1H, *dias*^{1}-*CH*(OH)CH_3), 4.77 (p, $^3J_{HH}$ = 6 Hz, 1H, *dias*^{2}-*CH*(OH)CH_3), 5.19 (s, 5H, *dias*^{2}-Cp), 5.23 (s, 5H, *dias*^{1}-Cp), 5.72 (s, 1H, *dias*^{1}-ArH), 5.83 (s, 1H, *dias*^{2}-ArH), 6.25 (s, 1H, *dias*^{2}-ArH), 6.34 (s, 1H, *dias*^{1}-ArH). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 0.80 (*dias*^{1}-TMS), 1.25 (*dias*^{2}-TMS), 22.18 (*dias*^{2}-CH_2), 22.23 (*dias*^{1}-CH_2), 22.3 (*dias*^{2}-CH_2), 22.4 (*dias*^{1}-CH_2), 25.0 (*dias*^{2}-CH(OH)CH_3), 26.3 (*dias*^{1}-CH(OH)CH_3), 27.9 (*dias*^{2}-CH_2), 28.2 (*dias*^{1}-CH_2), 28.3 (*dias*^{1}, *dias*^{2}-CH_2), 66.0 (*dias*^{1}-CH(OH)CH_3), 67.8 (*dias*^{2}-CH(OH)CH_3), 80.99 (*dias*^{2}-Cp), 81.18 (*dias*^{1}-Cp), 82.4 (*dias*^{1}-$C_{Ar}H$), 84.4 (*dias*^{2}-$C_{Ar}H$),

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88.5 (*dias*^{1}-C_{Ar}H), 89.2 (*dias*^{2}-C_{Ar}H), 93.4 (*dias*^{1}, *dias*^{2}-C_{Ar}), 102.85 (*dias*^{1}-C_{Ar}), 102.88 (*dias*^{2}-C_{Ar}), 103.1 (*dias*^{1}-C_{Ar}), 103.3 (*dias*^{2}-C_{Ar}), 111.9 (*dias*^{2}-C_{Ar}), 114.6 (*dias*^{1}-C_{Ar}). HRMS-(EI) (*m*/*z*): $[M + H]^+$ calcd for $C_{20}H_{29}ORuSi.F_6P$, 409.1058; found, 409.1062.

6-(1-(Trimethylsilyoxy)ethyl)tetralin (14-*Aryl*). $NaBH_4$ (671 mg, 17.76 mmol) was added to a stirred solution of 6-acetyltetralin (1.02 g, 5.92 mmol) in THF/MeOH (60 mL, 1/1) at 23 °C. After it was stirred for 30 min at 23 °C, the reaction mixture was then poured over acetone (50 mL), concentrated, diluted with H_2O (150 mL), and extracted with Et_2O (150 mL). The organic extracts were washed with brine (150 mL), dried over Na_2SO_4, and concentrated to afford a pale yellow oil. Chlorotrimethylsilane (0.090 mL, 0.920 mmol) was added to a stirred solution of the resulting oil (54 mg, 0.310 mmol) and triethylamine (0.130 mL, 0.920 mmol) in CH_2Cl_2 (3.1 mL) at 23 °C. After 2 h of stirring at 23 °C, the reaction mixture was poured over water (3 mL) and extracted. The organic extract was washed with water (3 mL) and brine (3 mL), dried over $MgSO_4$, and concentrated to afford **14**-*Aryl* as a yellow oil (69 mg, 90% yield for second step). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.08 (s, 9H, TMS), 1.41 (d, $^3J_{HH}$ = 6.5 Hz, 3H, CH(OTMS)CH_3), 1.73−1.84 (m, 4H, 2,3-CH_2), 2.69−2.83 (m, 4H, 1,4-CH_2), 4.79 (q, $^3J_{HH}$ = 6.5 Hz, 1H, C*H*(OTMS)CH_3), 6.99−7.07 (m, 3H, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 0.30 (TMS), 23.4 (2 × CH_2), 27.0 (CH(OTMS)CH_3), 29.2 (CH_2), 29.6 (CH_2), 70.6 (*C*H(OTMS)CH_3), 122.7 (C_{Ar}H), 126.1 (C_{Ar}H), 129.0 (C_{Ar}H), 135.7 (C_{Ar}), 136.9 (C_{Ar}), 143.6 (C_{Ar}). HRMS-(EI) (*m*/*z*): $[M + H]^+$ calcd for $C_{15}H_{24}OSi$, 248.1591; found, 248.1588.

(η^5-Pentamethylcyclopentadienyl)(η^6-6-(1-trimethylsiloxyethyl)-tetralinyl)ruthenium(II) Hexafluorophosphate (14-*Cp-*maj*).** **1**-*Cp** (21 mg, 0.042 mmol) was added to a solution of **14**-*Aryl* (10 mg, 0.042 mmol) in acetone-d_6 (0.42 mL) at 23 °C in a glovebox. After 15.5 h at 23 °C, the reaction mixture was concentrated and purified by flash column chromatography (alumina, CH_2Cl_2) followed by crystallization (CH_2Cl_2/Et_2O) to afford a mixture of **14**-*Cp**-*maj* and **14**-*Cp**-*min* as a colorless solid (16 mg, 61% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.24 (s, 9H, TMS), 1.50 (d, $^3J_{HH}$ = 6 Hz, 3H, CH(OTMS)CH_3), 1.85 (s, 15H, Cp*), 1.60−1.90 (m, 4H, 2,3-CH_2), 2.34−2.47 (m, 2H, 1,4-CH_{syn}), 2.69−2.82 (m, 2H, 1,4-CH_{anti}), 4.67 (q, $^3J_{HH}$ = 6 Hz, 1H, C*H*(OTMS)CH_3), 5.65 (s, 1H, 5-ArH), 5.68 (d, $^3J_{HH}$ = 6 Hz, 1H, ArH), 5.74 (d, $^3J_{HH}$ = 6 Hz, 1H, ArH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 1.1 (TMS), 10.2 (CpCH_3), 21.8 (CH_2), 21.9 (CH_2), 25.8, 26.3, 27.2 (2 × CH_2, CH(OTMS)CH_3), 67.6 (*C*H(OTMS)CH_3), 83.0 (C_{Ar}H), 83.4 (C_{Ar}H), 86.8 (C_{Ar}H), 94.7 (*C*pCH$_3$), 100.3 (C_{Ar}), 101.4 (C_{Ar}), 108.8 (C_{Ar}). HRMS-(ESI) (*m*/*z*) as mixture of **14**-*Cp**: $[M + H]^+$ calcd for $C_{25}H_{39}ORuSi.F_6P$, 479.1841; found, 479.1832.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00679.

NMR spectra, crystallographic data, and an index of compounds to aid the reader (PDF)

All computed molecule Cartesian coordinates (XYZ)

Accession Codes

CCDC 1572947−1572954 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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