Enantioface-Selective Coordination of Prochiral 1,3-Dienes to Planar-Chiral Cyclopentadienyl-Ruthenium Complexes

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The treatment of planar-chiral (η^5:η^1-cyclopentadienylphosphine)bis(acetonitrile)ruthenium complexes **1** with prochiral dienes led to the ligand-exchange reaction that gave (η^5:η^1-cyclopentadienylphosphine)(η^4-diene)ruthenium complexes **4**−**6** and **8**−**11** with high enantioface selectivity (up to >99% de). The configuration of the (η^4-diene)ruthenium complexes was determined by crystallographic study of (η^4-isoprene)ruthenium complex **6b-I** and spectral analyses, including NOE measurements. The selectivity of the reaction is under thermodynamic control of the resulting η^4-diene complexes and is affected by the substituents on both the cyclopentadienyl ligand and the diene.

Introduction

Enantioselective reactions mediated or catalyzed by transition-metal complexes have attracted much attention in synthetic organic chemistry.[1] Many asymmetric reactions of prochiral olefins with excellent enantioselectivity have been developed so far. In those reactions, the π-complexation of olefins with metal atoms inducing planar chirality is an important step for the development of new asymmetric reactions and the elucidation of reaction mechanisms. Therefore, there is rich stereochemistry in the coordination of prochiral olefins to chiral transition-metal fragments.[2,3] 1,3-Diene, which often shows unique reactivities different from those of simple olefins in the coordination sphere of transition metals, has been used as a starting material in enantioselective organic synthesis.[4] Planar-chiral 1,3-diene complexes are good chiral synthons for preparing natural products.[5] Although it has been reported that somechiral auxiliary on diene works effectively in diastereoselective π-complexation,[6] few studies have been conducted on enantioface selectivity in the complexation of prochiral dienes with chiral metal fragments.[7]

We have long been involved in the studies of planar-chiral cyclopentadienylruthenium (Cp′Ru) complexes.[8] One of our first efforts was to examine enantioface-selective π-complexation of arenes with the ruthenium center, where we found moderate selectivity under control of the planar chirality.[9] However, the rotation of the cyclopentadienyl ring was inadequate for the construction of a rigid chiral environment around the active metal center. We recently synthesized planar-chiral Cp′Ru complexes **1** possessing an anchor phosphine ligand.[10] Complex **1** showed high ability to control the metal-centered chirality in some ligand-exchange reactions[11] and was successfully used as a new catalyst for asymmetric allylic amination and alkylation with high enantioselectivity.[12] Moreover, as the cationic ruthenium complexes $[CpRuL(CH_3CN)_2]^+$ (L = CO, PR_3)

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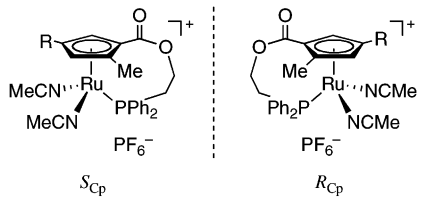
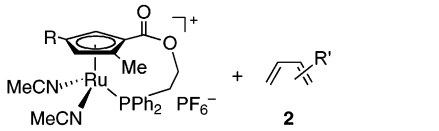
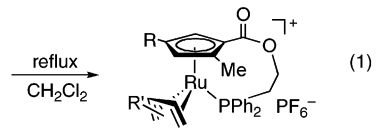
Chart 1. Enantiomeric Pair of Planar-Chiral Cp′-Ru Complex 1



undergo replacement of the acetonitrile ligands with a variety of dienes to give stable π-diene complexes [CpRuL(η^4-diene)],[13] we investigated the complexation of Cp′Ru complex **1** with prochiral dienes. We report herein the complete details of the enantioface-selective π-complexation of dienes with the ruthenium atom in planar-chiral Cp′Ru complexes. The preliminary results have already been reported elsewhere.[14] Although we used racemic mixtures of planar-chiral Cp′Ru complexes in this work, all structures are shown with a planar chirality of S_{Cp} for clarity.



1a: R = Me
1b: R = Ph
1c: R = *t*-Bu



(1)

3-6, 8-11

Results and Discussion

We started our investigation with the reaction of bis(acetonitrile) complex **1** with symmetrical diene. Treatment of complex **1a** with 10 equiv of 2,3-dimethylbutadiene **2a** in refluxing dichloromethane for 12 h resulted in the ligand-exchange reaction that gave diene-coordinated complex **3a** in good yield (eq 1). In the ^{1}H NMR spectrum of **3a**, two singlets ascribable to the methyl groups on the diene were observed at δ 2.44 and 2.45. The signals for the two sets of *syn*-protons (H^1, H^4) and *anti*-protons (H^2, H^3) on the terminal methylene with respect to the methyl groups appeared at δ 3.31, 3.19 and δ −0.39, −0.58, respectively. These data clearly showed that two H_2C═CMe− parts of the diene are not magnetically equivalent due to their coordination to the planar-chiral ruthenium complex. On the other hand, the reactions of complex **1a** with 2,5-dimethyl-2,4-hexadiene **2b** and 1,3-cyclohexadiene **2c** gave no diene complexes, and complex **1a** was recovered quantitatively. Then, we performed the reactions with unsymmetrical diene, and the results are summarized in Table 1. The treatment of complex **1a** with *trans*-1,3-pentadiene **2d** gave a diastereomeric mixture of η^4-diene complex **4a** in 93% yield (entry 1). The ^{1}H and ^{31}P NMR spectra of **4a** indicated that the diastereoselectivity is 34% de. Similarly, the reaction with *trans*-1,3-hexadiene **2e** gave diene complex **5a** in 93% yield with 38% de (entry 2). On the other hand, higher selectivity was observed in the reaction with isoprene **2f** (entry 3), whereas no diene complex was formed in the reaction with *cis*-1,3-pentadiene **2g** (entry 4). These results, as well as those from the reactions with **2b** and **2c** described above, suggest that the *Z*-substituted dienes do not coordinate to the ruthenium atom in complex **1a**. On the other hand, the reaction with 1-phenyl-1,3-butadiene **2h** gave η^4-diene complex **8a** with 76% de (entry 5), and that with 2-phenyl-1,3-butadiene **2i** produced complex **9a** with 86% de (entry 6). Disubstituted dienes, 2-methyl-1,3-pentadiene **2j** and 3-methyl-1,3-pentadiene **2k**, also reacted with complex **1a** to give complexes **10a** and **11a** with 83 and 48% de, respectively

Chart 2. Structures of Dienes

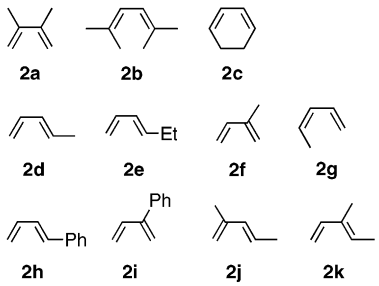


Chart 3. Numbering of H Atoms on Diene Ligands

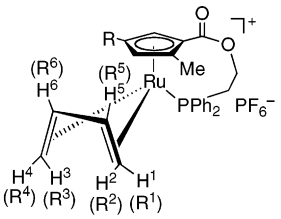


Table 1. Reaction of Ruthenium Complexes 1 with Prochiral Dienes

entry	substrate	diene	product	yield/%[a]	de/%[b,c]
1	**1a** (R = Me)	**2d**	**4a**	93	34 (I)
2	**1a**	**2e**	**5a**	93	38 (I)
3	**1a**	**2f**	**6a**	90	82 (I)
4	**1a**	**2g**	**7a**	0	
5	**1a**	**2h**	**8a**	72	76 (II)
6	**1a**	**2i**	**9a**	87	86 (I)
7	**1a**	**2j**	**10a**	88	83 (I)
8	**1a**	**2k**	**11a**	90	48 (I)
9	**1b** (R = Ph)	**2d**	**4b**	86	36 (I)
10	**1b**	**2e**	**5b**	88	36 (I)
11	**1b**	**2f**	**6b**	90	86 (I)
12	**1b**	**2h**	**8b**	92	>99 (II)
13	**1b**	**2i**	**9b**	92	81 (I)
14	**1b**	**2j**	**10b**	87	75 (I)
15	**1b**	**2k**	**11b**	85	38 (I)
16	**1c** (R = Bu^t)	**2d**	**4c**	74	66 (I)
17	**1c**	**2e**	**5c**	92	58 (I)
18	**1c**	**2f**	**6c**	69	84 (I)
19	**1c**	**2h**	**8c**	0	
20	**1c**	**2i**	**9c**	91	98 (I)
21	**1c**	**2j**	**10c**	0	
22	**1c**	**2k**	**11c**	82	84 (I)

[a] Isolated yield. [b] Determined by ^{31}P NMR. [c] The structure of the major product is given in parentheses; see Chart 5.

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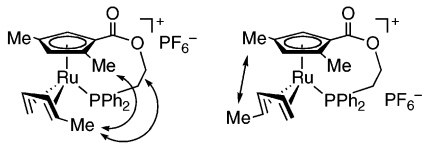
Chart 4. NOE in Complexes 4a-I and 4a-II



Major Product **4a-I** Minor Product **4a-II**

(entries 7 and 8). The reactions of complex **1b** bearing a phenyl group at the 4-position of the Cp′ ring also produced η^4-diene complexes having diastereoselectivities similar to those in the reactions of **1a** (entries 9−15). It is noteworthy that the η^4-diene complex **8b** was formed as a single diastereomer in the reaction with **2h** (entry 12). When complex **1c**, which is a *tert*-butyl analogue of complexes **1a** and **1b**, was used as the starting material, η^4-diene complexes were obtained with slightly higher selectivities than those of **1a** and **1b** (entries 16−22). However, dienes **2h** and **2j** did not coordinate to the ruthenium atom of **1c** (entries 19 and 21).

The stereochemistry of the major isomer of isoprene complex **6b-I** was unequivocally established by X-ray analysis to be $S_{Cp},R_{diene}/R_{Cp},S_{diene}$ (Figure 1).[15] The *s-cis* diene coordinates to the ruthenium in a prone (endo) fashion,[16] which is the major geometry in Cp(η^4-diene)-RuL complexes.[17] The ^{1}H NMR spectrum of **6b-I** exhibited signals ascribable to H^5 and CH_3 protons at δ 6.10 and 2.74, respectively. Whereas multiplet signals due to the *syn*-protons (H^1 and H^4) of the terminal methylene with respect to H^5 and CH_3 were found at δ 3.53−3.32, the *anti*-proton (H^2 and H^3) signals appeared in the higher magnetic field (δ −0.17, −0.29), as observed in complex **3a**. The molecular structure of **6b-I** indicates that the shift to the higher magnetic field of the *anti*-proton signals is probably caused by shielding due to the phenyl ring C(16)−C(21) protruding axially from the anchor phosphine. As a similar shift to the higher magnetic field of the signals due to the *anti*-diene protons was observed in the ^{1}H NMR spectrum of all other η^4-diene complexes prepared in this study (see Experimental Section), the diene ligands were assumed to coordinate in an *s-cis* prone fashion in these complexes. The fact that dienes having a substituent at the *anti*-position, such as **2b**, **2c**, and **2f**, did not produce any η^4-diene complexes is consistent with the estimated coordination mode of the diene ligands. To obtain

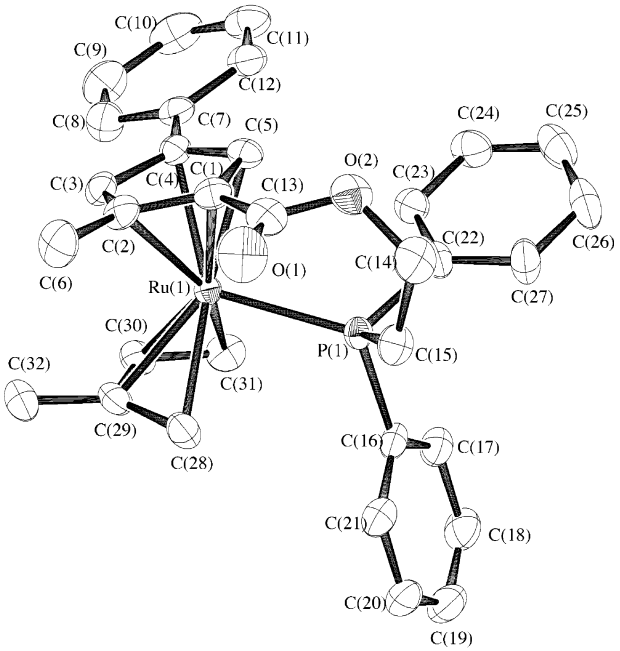
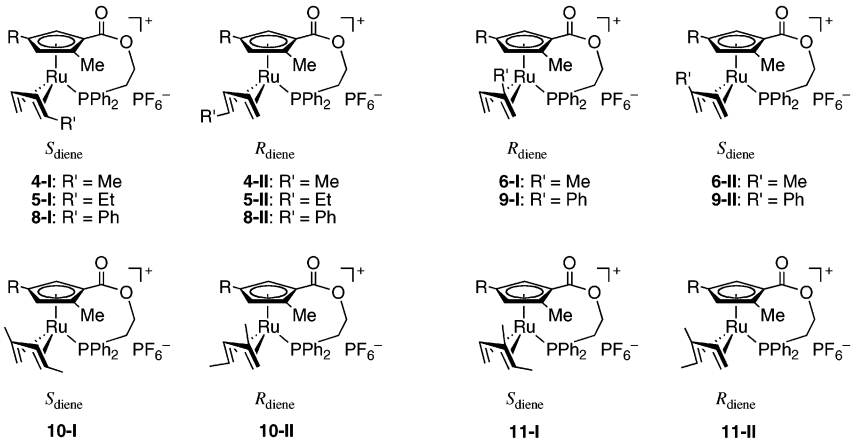


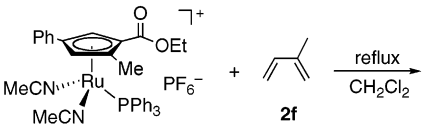
Figure 1. Molecular structure of the cation of **6b-I**·1.5Me_2CO. Hydrogen atoms, PF_6^- counteranion, and Me_2CO solvates are omitted for clarity.

information on the configuration of the products, differential NOE spectra were measured.[11b] For the major diastereomer of **4a**, irradiation of the methyl signal (δ 1.62) of the diene ligand gave rise to NOE signals of methyl protons at the 2-position of the Cp′ ring (δ 2.32) as well as the methylene protons of the tether (δ 3.23−3.29) but not the olefinic protons of the diene. On the other hand, NOE was observed between the methyl group on the diene ligand (δ 1.59) and the methyl group at the 4-position of the Cp′ ring (2.15 ppm) in the minor isomer. Altogether, these data suggest that the methyl group on the diene ligand is close to the 2-position of the Cp′ ring in the major isomer (**4a-I**), whereas it is close to the 4-position of the Cp′ ring in the minor isomer (**4a-II**). The stereochemistry of the other η^4-diene complexes was also determined from the differential NOE spectra. In most of the major isomers prepared from the monosubstituted dienes, the substituents were located close to the 2-position of the Cp′ ring (stereochemistry: **I**), with the exception of complexes **8a** and **8b**, which were prepared from 1-phenyl-1,3-butadiene **2h**. By

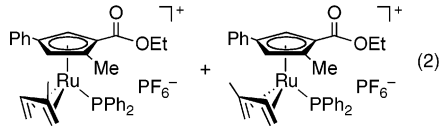
Chart 5. Conformational Structures of Diene Complexes



contrast, the major isomers prepared from disubstituted dienes were demonstrated to have configurations **10-I** and **11-I**, in which the C5 methyl carbon of the η^4-pentadiene is close to the 2-position of the Cp′ ring. As the ^{1}H NMR spectra of complex **5** are similar to those of **4**, the major product should adopt a conformation of **5-I**.



12



(2)

13

(83% yield, 44 %de)

The treatment of complex **12** having no tether between the Cp′ ring and the phosphine ligand with isoprene **2f** gave η^4-diene complex **13** in 83% yield. The diastereoselectivity was lower (44% de) than that in a similar reaction with **1b** (86% de, entry 11 in Table 1), although the stereochemistry of the major product could not be determined. This result clearly suggests that the anchor phosphine ligand actually prevents the rotation of the Cp′ ring and assists in the construction of an effective asymmetric environment by the planar chirality.[11,18]

When isoprene complex **6a** was dissolved in acetonitrile at room temperature, the isoprene ligand was completely replaced with two acetonitrile ligands to regenerate bis(acetonitrile) complex **1a** quantitatively, implying that the ligand-exchange reaction shown in eq 1 is reversible. Therefore, the selectivity of the reaction should be governed by the difference in thermodynamic stability between the two diastereomers of the η^4-diene complexes.

Some substituent effects on the diastereoselectivity of the diene coordination to the planar-chiral Cp′Ru complexes were found from the results in Table 1. Dienes possessing a substituent only at the 2-position, such as **2f** and **2i**, showed high selectivities in the reactions with the ruthenium complexes **1a**, **1b**, and **1c**. This may be due to the fact that the substituent on the diene at the 2-position is close to the Cp′ ring in a prone fashion. Complexes **6-II** and **9-II** should be less stable than complexes **6-I** and **9-I** because of the steric repulsion between the substituents on the dienes and on the Cp′ ring at the 4-position. The molecular structure of **6b-I** not only supports this explanation but also gives good information on the diastereoselectivity in the reactions with the other dienes. As observed in other planar-chiral Cp′Ru complexes, one of the two phenyl groups on the anchor phosphine is oriented axially, whereas the other phenyl ring protrudes equatorially.[10,11] The methyl and the ethyl groups on the dienes in complexes **4-II** and **5-II** are located in more crowded positions than those in **4-I** and **5-I**. Therefore, complexes **4-I** and **5-I** are formed as the major isomers in the reactions with **2d** and **2e**. In contrast, complex **8-II** was selectively obtained in the reaction with **2h**. The stability of **8b-II**, which was the sole product, may be explained by the $\pi-\pi$ stacking between the phenyl groups on the Cp′ ring and on the diene. On the other hand, the selective formation of **8a-II** may be derived from the CH$-\pi$ interaction between the methyl group at the 4-position of the Cp′ ring and the phenyl group on the diene,[19] as the ^{1}H NMR spectrum of **8a-II** exhibited a methyl signal at a slightly higher magnetic field (δ 1.60) than that of the other diene complexes. A similar contribution of the $\pi-\pi$ stacking and the CH$-\pi$ interaction to the diastereoselectivity has also been found in the salicylideneaminate derivatives.[11b] On the other hand, it remains unclear why 1,3-disubstituted diene **2j** showed higher selectivity than 1,2-disubstituted diene **2k**. As the *syn*-position of the terminal methylene group of the diene is very close to the axial phenyl ring on the anchor phosphine, the dienes with substituents at the *syn*-position, such as **2g**, **2b**, and **2c**, do not produce diene complexes at all.

There are no significant differences in the selectivity between complexes **1a** and **1b**, except for the reactions with **2h**. As can be observed in Figure 1, the phenyl ring lies on the same plane as the Cp′ ligand. Thus, the steric effect of the phenyl group is similar to that of the methyl group. In contrast, the higher diastereoselectivity in the reactions of complex **1c** is derived from the larger steric repulsion between the *tert*-butyl group and the substituents on the diene, which decreases the stability of structure **II**. Complex **1c** did not react with **2h** and **2j**, probably due to steric reasons.

In conclusion, we have demonstrated that the planar-chiral Cp′Ru complexes having the anchor phosphine ligand exhibit high enantioface selectivity in the π-complexation with prochiral dienes. The selectivity is controlled by the thermodynamic stability of the resulting diene complexes. These results should provide useful information for opening a new route for enantioselective synthesis from prochiral dienes using the planar-chiral Cp′Ru complexes.

Experimental Section

All reactions were carried out under argon atmosphere, but the workup was performed in air. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on JEOL JNM-LA400 and JEOL JNM-LA600 spectrometers using acetone-d_6 as solvent. Chemical shifts are given in ppm based on $SiMe_4$ as the internal standard for ^{1}H and ^{13}C NMR, and 85% H_3PO_4 as the external standard for ^{31}P NMR. IR spectra were recorded on a Perkin-Elmer system 2000 FT-IR. FAB mass spectra were obtained on a JEOL JMS-

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600H, and a JEOL JMS-700 was used for HRMS. Elemental analyses were performed by the Material Analysis Center, ISIR, Osaka University. Diethyl ether was distilled over benzophenone ketyl under argon immediately before use. Dichloromethane was distilled over calcium hydride. Ruthenium complexes **1** were prepared according to the method reported previously.[10] All other chemicals available commercially were used without further purification.

General Procedure of Ligand-Exchange Reaction of Ruthenium Complexes 1 with 1,3-Dienes. To a solution of ruthenium complex **1** (0.1 mmol) in dichloromethane (5 mL) was added diene (1.0 mmol), and the reaction mixture was stirred under reflux for 12 h. After removal of the solvent under reduced pressure, diethyl ether was added to the residual oil to give a yellow precipitate of a diene complex. The precipitate was filtered and washed with ether several times. Yield and diastereoselectivity of most of the products are listed in Table 1.

[(η^5:η^1-2,4-$Me_2C_5H_2CO_2CH_2CH_2PPh_2$)Ru{$\eta^4$-$CH_2$=C(Me)-C(Me)=$CH_2$}][$PF_6$] (3a). Yield: 86%. ^{1}H NMR (400 MHz): δ 8.02 (br, 2H, Ph), 7.75 (s, 3H, Ph), 7.42−7.38 (m, 3H, Ph), 7.08 (br, 2H, Ph), 5.27 (s, 1H, Cp′), 5.24−5.12 (m, 2H, Cp′ and OCH_2), 4.43−4.35 (m, 1H, OCH_2), 3.46−3.34 (m, 2H, PCH_2), 3.31 (s, 1H, H^1 or H^4), 3.19 (s, 1H, H^1 or H^4), 2.45 (s, 3H, Me on diene), 2.44 (s, 3H, Me on diene), 2.22 (d, 3H, J = 1.5 Hz, Cp′*Me*), 2.17 (s, 3H, Cp′*Me*), −0.39 (dd, 1H, J = 16.8, 2.0 Hz, H^2 or H^3), −0.58 (dd, 1H, J = 17.6, 2.0, Hz, H^2 or H^3). IR (cm^{-1}, KBr): 1721 ($\nu_{C=O}$). FAB MS: m/z 533 (M − PF_6^-). Anal. Calcd for $C_{28}H_{32}F_6O_2P_2Ru$: C, 49.63; H, 4.76. Found: C, 49.40; H, 4.50.

[(η^5:η^1-2,4-$Me_2C_5H_2CO_2CH_2CH_2PPh_2$)Ru($\eta^4$-$CH_2$=CHCH=CHMe)][$PF_6$] (4a). IR (cm^{-1}, KBr): 1731 ($\nu_{C=O}$). FAB MS: m/z 519 (M − PF_6^-). Anal. Calcd for $C_{27}H_{30}F_6O_2P_2Ru$: C, 48.87; H, 4.56; P, 9.53. Found: C, 48.66; H, 4.39; P, 9.53. For major product **4a-I**: ^{1}H NMR (400 MHz): δ 8.04−7.98 (m, 2H, Ph), 7.75−7.74 (m, 4H, Ph), 7.43 (m, 4H, Ph), 6.08−5.98 (m, 1H, H^5 or H^6), 5.81−5.75 (m, 2H, Cp′ and H^5 or H^6), 5.31−5.18 (m, 1H, OCH_2), 5.14−5.12 (m, 1H, Cp′), 4.48−4.41 (m, 1H, OCH_2), 3.43−3.24 (m, 2H, PCH_2), 3.11 (d, 1H, J = 8.1 Hz, H^4), 2.32 (d, 3H, J = 1.7 Hz, Cp′*Me*), 2.07 (s, 3H, Cp′*Me*), 1.62 (d, 3H, J = 5.3 Hz, Me on diene), 0.64−0.58 (m, 1H, H^2 or H^3), −0.22 to −0.28 (m, 1H, H^2 or H^3). ^{31}P NMR (160 MHz): δ 50.2. For minor product **4a-II**: ^{1}H NMR (400 MHz): δ 7.93−7.91 (m, 2H, Ph), 7.79−7.78 (m, 4H, Ph), 7.43 (m, 4H, Ph), 6.08−5.98 (m, 1H, Cp′), 5.81−5.75 (m, 1H, H^5 or H^6), 5.55 (m, 1H, H^5 or H^6), 5.43−5.41 (m, 1H, Cp′), 5.31−5.18 (m, 1H, OCH_2), 4.34−4.29 (m, 1H, OCH_2), 3.57−3.53 (m, 1H, PCH_2), 3.43−3.24 (m, 1H, PCH_2), 3.04 (d, 1H, J = 6.3 Hz, H^1), 2.18 (d, 3H, J = 1.7 Hz, Cp′*Me*), 2.15 (d, 3H, J = 1.7 Hz, Cp′*Me*), 1.59 (d, 3H, J = 4.6 Hz, Me on diene), 0.37−0.29 (m, 1H, H^2 or H^3), 0.19−0.13 (m, 1H, H^2 or H^3). ^{31}P NMR (160 MHz): δ 48.4.

[(η^5:η^1-2,4-$Me_2C_5H_2CO_2CH_2CH_2PPh_2$)Ru($\eta^4$-$CH_2$=CHCH=CHEt)][$PF_6$] (5a). IR (cm^{-1}, KBr): 1728 ($\nu_{C=O}$). FAB MS: m/z 533 (M − PF_6^-). Anal. Calcd for $C_{28}H_{32}F_6O_2P_2Ru$: C, 49.63; H, 4.76. Found: C, 49.48; H, 4.72. Major product **5a-I**: ^{1}H NMR (400 MHz): δ 8.03−7.45 (m, 10H, Ph), 6.01−5.98 (m, 1H, H^5 or H^6), 5.80 (dd, 1H, J = 9.5, 5.1 Hz, H^5 or H^6), 5.76 (s, 1H, Cp′), 5.30−5.15 (m, 1H, OCH_2), 5.14−5.13 (m, 1H, Cp′), 4.44−4.39 (m, 1H, OCH_2), 3.52−3.27 (m, 2H, PCH_2), 3.14 (d, 1H, J = 7.8 Hz, H^4), 2.31 (d, 3H, J = 1.7 Hz, Cp′*Me*), 2.08 (s, 3H, Cp′*Me*), 1.73−1.65 (m, 1H, CH_2CH$_3$), 1.05 (t, 3H, J = 7.3 Hz, CH$_2$CH_3), 0.56−0.48 (m, 1H, H^2 or H^3), −0.17 to −0.23 (m, 1H, H^2 or H^3). ^{31}P NMR (160 MHz): δ 49.9. For minor product **5a-II**: ^{1}H NMR (400 MHz): δ 8.03−7.45 (m, 10H, Ph), 6.07−6.05 (m, 1H, H^5 or H^6), 5.74 (s, 1H, Cp′), 5.55 (m, 1H, H^5 or H^6), 5.43−5.42 (m, 1H, Cp′), 5.30−5.15 (m, 1H, OCH_2), 4.36−4.29 (m, 1H, OCH_2), 3.52−3.27 (m, 2H, PCH_2), 3.04 (d, 1H, J = 7.1 Hz, H^1), 2.17 (s, 3H, Cp′*Me*), 2.16 (d, 3H, J = 1.7 Hz, Cp′*Me*), 1.73−1.65 (m, 1H, CH_2CH$_3$), 0.86 (t, 3H, J = 7.3 Hz, CH$_2$CH_3), 0.27−0.16 (m, 2H, H^2 and H^3). ^{31}P NMR (160 MHz): δ 48.5.

[(η^5:η^1-2,4-$Me_2C_5H_2CO_2CH_2CH_2PPh_2$)Ru{$\eta^4$-$CH_2$=CHC-(Me)=$CH_2$}][$PF_6$] (6a). IR (cm^{-1}, KBr): 1727 ($\nu_{C=O}$). FAB MS: m/z 519 (M − PF_6^-). Anal. Calcd for $C_{27}H_{30}F_6O_2P_2Ru$: C, 48.87; H, 4.56. Found: C, 48.63; H, 4.29. For major product **6a-I**: ^{1}H NMR (400 MHz): δ 8.29−8.24 (m, 2H, Ph), 8.03 (br, 3H, Ph), 7.72−7.64 (m, 3H, Ph), 7.40 (m, 3H, Ph), 6.10 (t, 1H, J = 8.5 Hz, H^6), 5.91 (s, 1H, Cp′), 5.55−5.43 (m, 2H, Cp′ and OCH_2), 4.70−4.62 (m, 1H, OCH_2), 3.76−3.66 (m, 2H, PCH_2), 3.55 (s, 1H, H^1 or H^4), 3.49−3.46 (m, 1H, H^1 or H^4), 2.74 (s, 3H, Me), 2.45 (d, 3H, J = 1.5 Hz, Me), 2.39 (s, 3H, Me), 0.04 to −0.03 (m, 2H, H^2 and H^3). ^{13}C NMR (150 MHz): δ 166.5 (C=O), 134.2−129.1 (Ph), 117.6, 110.1, 105.4, 93.9 (J = 5.0 Hz), 87.6, 87.5, 82.5, 59.6 (J = 5.8 Hz, OCH_2), 53.8 (C^1 or C^4), 52.2 (C^1 or C^4), 23.3 (PCH_2), 23.0 (Me on diene), 12.1 (Cp′*Me*), 11.5 (Cp′*Me*). ^{31}P NMR (160 MHz): δ 52.2. For minor product **6a-II**: ^{31}P NMR (160 MHz): δ 51.9.

[(η^5:η^1-2,4-$Me_2C_5H_2CO_2CH_2CH_2PPh_2$)Ru($\eta^4$-$CH_2$=CHCH=CHPh)][$PF_6$] (8a). IR (cm^{-1}, KBr): 1734 ($\nu_{C=O}$). FAB MS: m/z 581 (M − PF_6^-). Anal. Calcd for $C_{32}H_{32}F_6O_2P_2Ru$: C, 52.97; H, 4.45. Found: C, 52.69; H, 4.45. For major product **8a-II**: ^{1}H NMR (600 MHz): δ 7.69−7.23 (m, 15H, Ph), 6.82 (dd, 1H, J = 6.0, 10.7 Hz, H^5 or H^6), 5.87 (s, 1H, Cp′), 5.68−5.64 (m, 1H, H^5 or H^6), 5.16 (q, 1H, J = 1.6 Hz, Cp′), 5.14−5.07 (m, 1H, OCH_2), 4.42−4.37 (m, 1H, OCH_2), 3.46−3.31 (m, 3H, PCH_2 and H^1), 2.13 (d, 3H, J = 1.6 Hz, Cp′*Me*), 1.60 (s, 3H, Cp′*Me*), 1.56 (t, 1H, J = 10.7 Hz, H^2 or H^3), 0.81 (dd, 1H, J = 15.1, 10.2 Hz, H^2 or H^3). ^{31}P NMR (160 MHz): δ 45.3. For minor product **8a-I**: ^{31}P NMR (160 MHz): δ 47.4.

[(η^5:η^1-2,4-$Me_2C_5H_2CO_2CH_2CH_2PPh_2$)Ru{$\eta^4$-$CH_2$=CHC-(Ph)=$CH_2$}][$PF_6$] (9a). IR (cm^{-1}, KBr): 1733 ($\nu_{C=O}$). FAB MS: m/z 581 (M − PF_6^-). Anal. Calcd for $C_{32}H_{32}F_6O_2P_2Ru$: C, 52.97; H, 4.45. Found: C, 52.48; H, 4.18. For major product **9a-I**: ^{1}H NMR (600 MHz): δ 8.13−7.44 (m, 15H, Ph), 6.73 (t, 1H, J = 8.5 Hz, H^6), 5.24−5.13 (m, 3H, Cp′ and OCH_2), 4.44 (ddd, 1H, J = 11.5, 5.5, 2.2 Hz, OCH_2), 4.20 (s, 1H, H^1 or H^4), 3.53−3.37 (m, 3H, PCH_2 and H^1 or H^4), 2.18 (s, 3H, Cp′*Me*), 1.02 (d, 3H, J = 1.4 Hz, Cp′*Me*), −0.08 (ddd, 1H, J = 15.1, 9.3, 2.2 Hz, H^2 or H^3), −0.32 (dd, 1H, J = 16.2, 2.5 Hz, H^2 or H^3). ^{31}P NMR (160 MHz): δ 52.4. For minor product **9a-II**: ^{31}P NMR (160 MHz): δ 51.5.

[(η^5:η^1-2,4-$Me_2C_5H_2CO_2CH_2CH_2PPh_2$)Ru{$\eta^4$-$CH_2$=C(Me)-CH=CHMe}][$PF_6$] (10a). IR (cm^{-1}, KBr): 1725 ($\nu_{C=O}$). FAB MS: m/z 533 (M − PF_6^-). Anal. Calcd for $C_{28}H_{32}F_6O_2P_2Ru$: C, 49.63; H, 4.76. Found: C, 49.41; H, 4.51. For major product **10a-I**: ^{1}H NMR (600 MHz): δ 8.03−7.42 (m, 10H, Ph), 5.66 (d, 1H, J = 9.3 Hz, H^5), 5.35 (s, 1H, Cp′), 5.23 (ddd, 1H, J = 11.5, 11.5, 8.0 Hz, OCH_2), 5.12 (s, 1H, Cp′), 4.45 (ddt, 1H, J = 11.5, 5.2, 1.9 Hz, OCH_2), 3.36 (dt, 1H, J = 15.7, 5.2 Hz, PCH_2), 3.28−3.20 (m, 1H, PCH_2), 3.16 (t, 1H, J = 1.4 Hz, H^4), 2.50 (s, 3H, Me on diene), 2.37 (s, 3H, Cp′*Me*), 2.15 (s, 3H, Cp′*Me*), 1.62 (dd, 3H, J = 6.0, 0.8 Hz, Me on diene), 0.47 (dq, 1H, J = 15.4, 6.0 Hz, H^2 or H^3), −0.46 (dd, 1H, J = 16.2, 1.9 Hz, H^2 or H^3). ^{31}P NMR (160 MHz): δ 51.2. For minor product **10a-II**: ^{31}P NMR (160 MHz): δ 49.5.

[(η^5:η^1-2,4-$Me_2C_5H_2CO_2CH_2CH_2PPh_2$)Ru{$\eta^4$-$CH_2$=CHC-(Me)=CHMe}] [$PF_6$] (11a). IR (cm^{-1}, KBr): 1731 ($\nu_{C=O}$). FAB MS: m/z 533 (M − PF_6^-). Anal. Calcd for $C_{28}H_{32}F_6O_2P_2Ru$: C, 49.63; H, 4.76. Found: C, 49.35; H, 4.80. For major product **11a-I**: ^{1}H NMR (600 MHz): δ 7.92−7.42 (m, 10H, Ph), 5.78 (t, 1H, J = 8.3 Hz, H^6), 5.59 (s, 1H, Cp′), 5.23 (ddd, 1H, J = 22.5, 11.5, 7.6 Hz, OCH_2), 5.04 (s, 1H, Cp′), 4.40 (ddt, 1H, J = 11.5, 5.2, 1.9 Hz, OCH_2), 3.49−3.24 (m, 2H, PCH_2), 3.06 (d, 1H, J = 8.3 Hz, H^4), 2.42 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 1.56 (dd, 3H, J = 6.3, 1.4 Hz, CH_3), 0.23 (dq, 1H, J = 21.7, 6.3 Hz, H^2 or H^3), −0.25 (ddd, 1H, J = 15.9, 9.9, 2.2 Hz, H^2 or H^3). ^{31}P NMR (160 MHz): δ 51.3. For minor product **11a-II**: ^{1}H NMR (400 MHz): δ 7.92−7.42 (m, 10H, Ph), 5.52 (t, 1H, J = 8.3 Hz, H^5), 5.35 (s, 1H, Cp′), 5.31 (s, 1H, Cp′), 5.15 (ddd, 1H, J = 23.3, 11.5, 7.6 Hz, OCH_2), 4.32 (ddt, 1H, J = 11.5, 4.9, 2.2 Hz, OCH_2), 3.49−3.24 (m, 2H, PCH_2), 2.93 (dd, 1H, J = 8.3, 1.9 Hz, H^1), 2.42 (s, 3H, CH_3), 2.21 (s, 3H, CH_3),

2.14 (s, 3H, CH_3), 1.52 (dd, 3H, J = 6.3, 1.6 Hz, CH_3), 0.07 (ddd, 1H, J = 15.4, 9.3, 2.2 Hz, H^2 or H^3), 0.01 (dq, 1H, J = 21.2, 6.3 Hz, H^2 or H^3). ^{31}P NMR (160 MHz): δ 49.2.

[(η^5:η^1-2-Me-4-Ph$C_5H_2CO_2CH_2CH_2PPh_2$)Ru(η^4-CH_2=CHCH=CHMe)][PF_6] (4b). IR (cm^{-1}, KBr): 1732 ($\nu_{C=O}$). FAB MS: m/z 581 (M − PF_6^-). Anal. Calcd for $C_{32}H_{32}F_6O_2P_2Ru$: C, 52.97; H, 4.45. Found: C, 52.71; H, 4.22. For major product **4b-I**: ^{1}H NMR (400 MHz): δ 7.90−7.40 (m, 15H, Ph), 6.46 (s, 1H, Cp′), 6.14−6.09 (m, 1H, H^5 or H^6), 5.88 (dd, 1H, J = 10.3, 5.6 Hz, H^5 or H^6), 5.76 (dd, 1H, J = 4.2, 2.4 Hz, Cp′), 5.37−5.19 (m, 1H, OCH_2), 4.54 (dq, 1H, J = 4.2, 2.4 Hz, OCH_2), 3.46−3.24 (m, 2H, PCH_2), 2.79 (s, 1H, H^4), 2.45 (d, 3H, J = 1.7 Hz, Cp′*Me*), 1.64 (d, 3H, J = 6.1 Hz, Me on diene), 0.72−0.61 (m, 1H, H^2 or H^3), −0.26 (dd, 1H, J = 12.2, 11.0 Hz, H^2 or H^3). ^{31}P NMR (160 MHz): δ 50.8. For minor product **4b-II**: ^{1}H NMR (400 MHz): δ 7.90−7.40 (m, 15H, Ph), 6.54 (s, 1H, Cp′), 6.05 (dd, 1H, J = 4.2, 2.4 Hz, Cp′), 5.96 (dd, 1H, J = 10.3, 5.6 Hz, H^5 or H^6), 5.73−5.69 (m, 1H, H^5 or H^6), 5.37−5.19 (m, 1H, OCH_2), 4.45 (dt, 1H, J = 5.4, 2.0 Hz, OCH_2), 3.46−3.24 (m, 2H, PCH_2), 3.05 (d, 1H, J = 6.8 Hz, H^1), 2.28 (d, 3H, J = 1.7 Hz, Cp′*Me*), 0.78 (dd, 3H, J = 6.1, 1.5 Hz, Me on diene), 0.35−0.25 (m, 1H, H^2 or H^3), −0.12 (dd, 1H, J = 10.5, 12.4 Hz, H^2 or H^3). ^{31}P NMR (160 MHz): δ 49.3.

[(η^5:η^1-2-Me-4-Ph$C_5H_2CO_2CH_2CH_2PPh_2$)Ru(η^4-CH_2=CHCH=CHEt)][PF_6] (5b). IR (cm^{-1}, KBr): 1733 ($\nu_{C=O}$). FAB MS: m/z 595 (M − PF_6^-). Anal. Calcd for $C_{33}H_{34}F_6O_2P_2Ru$: C, 53.59; H, 4.63. Found: C, 53.88; H, 4.69. For major product **5b-I**: ^{1}H NMR (400 MHz): δ 7.89−7.41 (m, 15H, Ph), 6.45 (s, 1H, Cp′), 6.12−6.06 (m, 1H, H^5 or H^6), 5.88 (dd, 1H, J = 9.8, 5.4 Hz, H^5 or H^6), 5.76 (dd, 1H, J = 3.9, 2.4 Hz, Cp′), 5.35−5.19 (m, 1H, OCH_2), 4.53 (ddt, 1H, J = 9.3, 5.1, 2.2 Hz, OCH_2), 3.47−3.29 (m, 2H, PCH_2), 3.05 (d, 1H, J = 8.1 Hz, H^1), 2.44 (d, 3H, J = 1.7 Hz, Cp′*Me*), 1.76−1.68 (m, 1H, CH_2CH$_3$), 1.13−1.05 (m, 3H, CH$_2$CH_3), 0.26−0.22 (m, 1H, H^2 or H^3), −0.18 to −0.22 (m, 1H, H^2 or H^3). ^{31}P NMR (160 MHz): δ 50.6. Minor product **5b-II**: ^{1}H NMR (400 MHz): δ 7.89−7.41 (m, 15H, Ph), 6.52 (s, 1H, Cp′), 6.04 (dd, 1H, J = 3.4, 2.4 Hz, Cp′), 6.00 (dd, 1H, J = 9.8, 5.4 Hz, H^5 or H^6), 5.73−5.69 (m, 1H, H^5 or H^6), 5.35−5.19 (m, 1H, OCH_2), 4.39 (ddt, 1H, J = 9.5, 5.1, 2.2 Hz, OCH_2), 3.47−3.29 (m, 3H, PCH_2, H^1), 2.27 (d, 3H, J = 1.7 Hz, Cp′*Me*), 1.29−1.26 (m, 2H, CH_2CH$_3$), 0.65−0.53 (m, 4H, CH$_2$CH_3 and H^2 or H^3), 0.18−0.12 (m, 1H, H^2 or H^3). ^{31}P NMR (160 MHz): δ 49.4.

[(η^5:η^1-2-Me-4-Ph$C_5H_2CO_2CH_2CH_2PPh_2$)Ru{η^4-CH_2=CHC(Me)=CH_2}][PF_6] (6b). IR (cm^{-1}, KBr): 1727 ($\nu_{C=O}$). FAB MS: m/z 581 (M − PF_6^-). Anal. Calcd for $C_{32}H_{32}F_6O_2P_2Ru$: C, 52.97; H, 4.45. Found: C, 52.74; H, 4.25. For major product **6b-I**: ^{1}H NMR (400 MHz): δ 7.78−7.57 (m, 10H, Ph), 7.41−7.32 (m, 3H, Ph), 7.07 (br, 2H, Ph), 6.30 (d, 1H, J = 1.0 Hz, Cp′), 5.82−5.76 (m, 2H, H^6 and Cp′), 5.33−5.22 (m, 1H, OCH_2), 4.49 (ddt, 1H, J = 11.7, 5.6, 2.2 Hz, OCH_2), 3.53−3.36 (m, 3H, PCH_2 and H^1 or H^4), 3.32 (s, 1H, H^1 or H^4), 2.58 (s, 3H, CH_3), 2.30 (d, 3H, J = 1.5 Hz, CH_3), −0.17 (dd, 1H, J = 16.1, 2.0 Hz, H^2 or H^3), −0.29 (ddd, 1H, J = 15.9, 9.5, 2.2 Hz, H^2 or H^3). ^{13}C NMR (150 MHz): δ 166.3 (C=O), 134.3−127.9 (Ph), 111.2, 110.5, 106.3, 88.9 (J = 5.0 Hz), 87.6, 86.0, 83.5, 59.7 (J = 5.8 Hz, OCH_2), 53.5 (J = 4.1 Hz, C^1 or C^4), 53.3 (J = 4.1 Hz, C^1 or C^4), 23.2 (PCH_2), 22.9 (Me on diene), 11.65 (Cp′*Me*). ^{31}P NMR (160 MHz): δ 53.0. For minor product **6b-II**: ^{31}P NMR (160 MHz): δ 51.5.

[(η^5:η^1-2-Me-4-Ph$C_5H_2CO_2CH_2CH_2PPh_2$)Ru(η^4-CH_2=CHCH=CHPh)][PF_6] (8b). IR (cm^{-1}, KBr): 1731 ($\nu_{C=O}$). HRMS calcd for $C_{37}H_{34}O_2PRu$ (M − PF_6^-) 643.1340, found m/z 643.1332. ^{1}H NMR (600 MHz): δ 7.70−7.34 (m, 15H, Ph), 7.02 (t, 1H, J = 7.4 Hz, Ph), 6.68−6.64 (m, 3H, Ph, Cp′), 6.58 (dd, 1H, J = 11.0, 5.2 Hz, H^5 or H^6), 6.40 (d, 2H, J = 7.4 Hz, Ph), 5.81−5.76 (m, 2H, Cp′ and H^5 or H^6), 5.13 (ddd, 1H, J = 23.9, 12.4, 7.4 Hz, OCH_2), 4.39 (ddt, 1H, J = 11.8, 5.0, 2.5 Hz, OCH_2), 3.41−3.34 (m, 1H, PCH_2), 3.28−3.22 (m, 2H, PCH_2 and H^1), 2.21 (d, 3H, J = 1.4 Hz, Cp′*Me*), 1.40 (t, 1H, J = 11.0 Hz, H^2 or H^3), 0.62−0.58 (m, 1H, H^2 or H^3). ^{31}P NMR (160 MHz): δ 45.3.

[(η^5:η^1-2-Me-4-Ph$C_5H_2CO_2CH_2CH_2PPh_2$)Ru{η^4-CH_2=CHC(Ph)=CH_2}][PF_6] (9b). IR (cm^{-1}, KBr): 1738 ($\nu_{C=O}$). HRMS calcd for $C_{37}H_{34}O_2PRu$ (M − PF_6^-) 643.1340, found m/z 643.1360. For major product **9b-I**: ^{1}H NMR (600 MHz): δ 8.25−7.38 (m, 20H, Ph), 6.71 (t, 1H, J = 9.3 Hz, H^6), 5.82 (s, 1H, Cp′), 5.76 (q, 1H, J = 1.7 Hz, Cp′), 5.26 (ddd, 1H, J = 23.9, 11.5, 6.9 Hz, OCH_2), 4.52 (ddt, 1H, J = 11.5, 5.2, 2.2 Hz, OCH_2), 4.22 (s, 1H, H^1 or H^4), 3.57−3.45 (m, 2H, PCH_2), 2.61 (ddd, 1H, J = 8.0, 2.2, 1.4 Hz, H^1 or H^4), 1.09 (d, 3H, J = 1.7 Hz, CH_3), −0.08 (ddd, 1H, J = 15.1, 9.3, 2.2 Hz, H^2 or H^3), −0.21 (dd, 1H, J = 16.8, 2.7 Hz, H^2 or H^3). ^{31}P NMR (160 MHz): δ 53.0. For minor product **9b-II**: ^{31}P NMR (160 MHz): δ 51.8.

[(η^5:η^1-2-Me-4-Ph$C_5H_2CO_2CH_2CH_2PPh_2$)Ru{η^4-CH_2=C(Me)CH=CHMe}][PF_6] (10b). IR (cm^{-1}, KBr): 1733 ($\nu_{C=O}$). HRMS calcd for $C_{33}H_{34}O_2PRu$ (M − PF_6^-) 595.1340, found m/z 595.1339. For major product: **10b-I**: ^{1}H NMR (400 MHz): δ 7.95−7.39 (m, 15H, Ph), 6.12 (s, 1H, Cp′), 5.80 (dd, 1H, J = 4.1, 2.4 Hz, Cp′), 5.70 (d, 1H, J = 9.0 Hz, H^5), 5.29 (ddd, 1H, J = 22.7, 11.7, 7.1 Hz, OCH_2), 4.55 (ddt, 1H, J = 11.7, 5.1, 2.2 Hz, OCH_2), 3.46−3.25 (m, 2H, PCH_2), 2.74 (s, 1H, H^4), 2.48 (d, 3H, J = 1.7 Hz, Me), 2.45 (s, 3H, Me), 1.64 (d, 3H, J = 6.1 Hz, Me), 0.53−0.43 (m, 1H, H^2 or H^3), −0.44 (dd, 1H, J = 16.6, 2.2 Hz, H^2 or H^3). ^{31}P NMR (160 MHz): δ 50.7. For minor product **10b-II**: ^{1}H NMR (400 MHz): δ 7.95−7.39 (m, 15H, Ph), 6.34 (s, 1H, Cp′), 5.96 (t, 1H, J = 2.7 Hz, Cp′), 5.61 (d, 1H, J = 9.5 Hz, H^6), 5.22−5.17 (m, 1H, OCH_2), 4.40−4.32 (m, 1H, OCH_2), 3.46−3.25 (m, 2H, PCH_2), 3.11 (s, 1H, H^1), 2.58 (s, 3H, CH_3), 2.28 (d, 3H, J = 1.5 Hz, CH_3), 0.72 (dd, 3H, J = 6.1, 1.7 Hz, CH_3), 0.22−0.14 (m, 1H, H^2 or H^3), −0.10 to −0.14 (m, 1H, H^2 or H^3). ^{31}P NMR (160 MHz): δ 50.4.

[(η^5:η^1-2-Me-4-Ph$C_5H_2CO_2CH_2CH_2PPh_2$)Ru{η^4-CH_2=CHC(Me)=CHMe}][PF_6] (11b). IR (cm^{-1}, KBr): 1731 ($\nu_{C=O}$). HRMS calcd for $C_{33}H_{34}O_2PRu$ (M − PF_6^-) 595.1340, found m/z 595.1339. For major product **11b-I**: ^{1}H NMR (400 MHz): δ 7.88−7.39 (m, 15H, Ph), 6.29 (s, 1H, Cp′), 5.80 (t, 1H, J = 8.5 Hz, H^6), 5.66 (dd, 1H, J = 4.1, 2.4 Hz, Cp′), 5.29 (ddd, 1H, J = 22.7, 11.7, 7.3 Hz, OCH_2), 4.50 (ddt, 1H, J = 11.7, 5.1, 3.5 Hz, OCH_2), 3.49−3.30 (m, 2H, PCH_2), 2.55 (s, 3H, Me), 2.33 (d, 3H, J = 1.7 Hz, Me), 2.15 (d, 1H, J = 8.1 Hz, H^4), 1.57 (dd, 3H, J = 6.3, 1.5 Hz, Me), 0.34−0.25 (m, 1H, H^2 or H^3), −0.26 (ddd, 1H, J = 15.9, 9.8, 2.2 Hz, H^2 or H^3). ^{31}P NMR (160 MHz): δ 51.8. For minor product **11b-II**: ^{1}H NMR (400 MHz): δ 7.88−7.39 (m, 15H, Ph), 6.13 (s, 1H, Cp′), 6.01 (dd, 1H, J = 3.7, 2.4 Hz, Cp′), 5.56 (t, 1H, J = 8.2 Hz, H^5), 5.21−5.18 (m, 1H, OCH_2), 4.43−4.38 (m, 1H, OCH_2), 3.49−3.30 (m, 2H, PCH_2), 2.99 (d, 1H, J = 7.5 Hz, H^1), 2.39 (s, 3H, Me), 2.31 (d, 3H, J = 1.5 Hz, Me), 0.83 (dd, 3H, J = 6.1, 1.7 Hz, Me), 0.13−0.02 (m, 2H, H^2 and H^3). ^{31}P NMR (160 MHz): δ 49.3.

[(η^5:η^1-2-Me-4-Bu^t$C_5H_2CO_2CH_2CH_2PPh_2$)Ru(η^4-CH_2=CHCH=CHMe)][PF_6] (4c). IR (cm^{-1}, KBr): 1731 ($\nu_{C=O}$). FAB MS: m/z 561 (M − PF_6^-). Anal. Calcd for $C_{30}H_{36}F_6O_2P_2Ru$: C, 51.07; H, 5.14. Found: C, 50.80; H, 5.05. For major product **4c-I**: ^{1}H NMR (400 MHz): δ 8.18−8.13 (m, 2H, Ph), 7.76−7.65 (m, 4H, Ph), 7.41 (br, 4H, Ph), 6.14−6.07 (m, 1H, H^5 or H^6), 5.85 (s, 1H, Cp′), 5.74 (dd, 1H, J = 9.8, 5.4 Hz, H^5 or H^6), 5.33−5.22 (m, 2H, CpH, OCH_2), 4.44−4.40 (m, 1H, OCH_2), 3.71 (d, 1H, J = 7.8 Hz, H^4), 3.42−3.24 (m, 2H, PCH_2), 2.33 (d, 3H, J = 1.7 Hz, Cp′Me), 1.64 (d, 3H, J = 6.1 Hz, Me on diene), 1.34 (s, 9H, Bu^t), 0.59−0.50 (m, 1H, H^2 or H^3), −0.29 to −0.35 (m, 1H, H^2 or H^3). ^{31}P NMR (160 MHz): δ 46.3. For minor product **4c-II**: ^{1}H NMR (400 MHz): δ 8.18−8.13 (m, 2H, Ph), 7.76−7.65 (m, 4H, Ph), 7.41 (br, 4H, Ph), 6.14−6.07 (m, 1H, H^5 or H^6), 5.83 (s, 1H, Cp′), 5.55 (t, 1H, J = 2.4 Hz, Cp′), 5.33−5.22 (m, 2H, H^5 or H^6 and OCH_2), 4.44−4.40 (m, 1H, OCH_2), 3.42−3.24 (m, 2H, PCH_2), 2.12 (d, 3H, J = 2.2 Hz, Cp′*Me*), 1.77 (d, 3H, J = 1.7, 6.1 Hz, Me on diene), 1.42 (s, 9H, Bu^t),

0.42−0.35 (m, 1H, H^2 or H^3), 0.16−0.10 (m, 1H, H^2 or H^3). ^{31}P NMR (160 MHz): δ 46.1.

[(η^5:η^1-2-Me-4-Bu^{t}C$_5$H$_2$CO$_2$CH$_2$CH$_2$PPh$_2$)Ru(η^4-CH$_2$=CHCH=CHEt)] [PF$_6$] (5c). IR (cm^{-1}, KBr): 1733 ($\nu_{C=O}$). FAB MS: *m*/*z* 575 (M − PF_6^-). Anal. Calcd for $C_{31}H_{38}F_6O_2P_2Ru$: C, 51.74; H, 5.32. Found: C, 51.50; H, 5.08. For major product **5c-I**: ^{1}H NMR (400 MHz): δ 8.18−8.13 (m, 2H, Ph), 7.78−7.42 (m, 8H, Ph), 6.12−6.08 (m, 1H, H^5 or H^6), 5.83 (s, 1H, Cp′), 5.73 (dd, 1H, J = 9.5, 5.1 Hz, H^5 or H^6), 5.32−5.22 (m, 2H, Cp′ and OCH_2), 4.45−4.38 (m, 1H, OCH_2), 3.74 (d, 1H, J = 7.8 Hz, H^4), 3.52−3.29 (m, 2H, PCH_2), 2.32 (d, 3H, J = 1.7 Hz, Cp′*Me*), 1.82−1.70 (m, 2H, CH_2CH$_3$), 1.34 (s, 9H, Bu^t), 1.05 (t, 3H, J = 7.3 Hz, CH$_2$CH_3), 0.50−0.40 (m, 1H, H^2 or H^3), −0.23 to −0.30 (m, 1H, H^2 or H^3). ^{31}P NMR (160 MHz): δ 46.0. For minor product **5c-II**: ^{1}H NMR (400 MHz): δ 8.18−8.13 (m, 2H, Ph), 7.78−7.42 (m, 8H, Ph), 6.12−6.08 (m, 1H, H^5 or H^6), 5.80 (s, 1H, Cp′), 5.55−5.53 (m, 2H, Cp′ and H^5 or H^6), 5.16−5.12 (m, 1H, OCH_2), 4.26−4.18 (m, 1H, OCH_2), 3.52−3.29 (m, 2H, PCH_2), 2.97 (d, 1H, J = 5.9 Hz, H^1), 2.12 (d, 3H, J = 1.5 Hz, Cp′*Me*), 1.82−1.70 (m, 2H, CH_2CH$_3$), 1.40 (s, 9H, Bu^t), 0.84 (t, 3H, J = 7.3 Hz, CH$_2$CH_3), 0.32−0.30 (m, 1H, H^2 or H^3), 0.17−0.14 (m, 1H, H^2 or H^3). ^{31}P NMR (160 MHz): δ 46.2.

[(η^5:η^1-2-Me-4-Bu^{t}C$_5$H$_2$CO$_2$CH$_2$CH$_2$PPh$_2$)Ru{η^4-CH$_2$=CHC(Me)=CH$_2$}][PF$_6$] (6c). IR (cm^{-1}, KBr): 1733 ($\nu_{C=O}$). FAB MS: *m*/*z* 561 (M − PF_6^-). Anal. Calcd for $C_{30}H_{36}F_6O_2P_2Ru$: C, 51.07; H, 5.14. Found: C, 50.80; H, 5.06. For major product **6c-I**: ^{1}H NMR (400 MHz): δ 8.16−8.11 (m, 2H, Ph), 7.76−7.66 (m, 3H, Ph), 7.44−7.35 (m, 3H, Ph), 7.13 (br, 2H, Ph), 5.90 (t, 1H, J = 8.8 Hz, H^6), 5.67 (s, 1H, Cp′), 5.28−5.17 (m, 2H, Cp′ and OCH_2), 4.41−4.33 (m, 1H, OCH_2), 3.81−3.78 (m, 1H, H^1 or H^4), 3.43−3.38 (m, 2H, PCH_2), 3.21 (s, 1H, H^1 or H^4), 2.47 (d, 3H, J = 0.7 Hz, CH_3), 2.21 (d, 3H, J = 1.5 Hz, CH_3), 1.37 (s, 9H, Bu^t), −0.18- −0.23 (m, 1H, H^2 or H^3), −0.30 to −0.37 (m, 1H, H^2 or H^3). ^{13}C NMR (acetonitrile-d_3, 150 MHz): δ 167.6 (C=O), 135.8−124.8 (Ph), 109.0 (J = 14 Hz), 89.8 (J = 4 Hz), 88.2 (J = 14 Hz), 83.1, 82.5, 60.2 (J = 5 Hz), 53.7 (J = 5 Hz), 49.5, 33.5 (*C*Me$_3$), 31.4 (C*Me*$_3$), 23.4 (d, J = 31 Hz, PCH_2), 23.2 (Me), 12.0 (Me). ^{31}P NMR (160 MHz): δ 48.8. For minor product **6c-II**: ^{31}P NMR (160 MHz): δ 47.4.

[(η^5:η^1-2-Me-4-Bu^{t}C$_5$H$_2$CO$_2$CH$_2$CH$_2$PPh$_2$)Ru{η^4-CH$_2$=CHC(Ph)=CH$_2$}][PF$_6$] (9c). IR (cm^{-1}, KBr): 1735 ($\nu_{C=O}$). HRMS calcd for $C_{35}H_{38}O_2PRu$ (M − PF_6^-) 623.1653, found *m*/*z* 623.1645. For major product **9c-I**: ^{1}H NMR (400 MHz): δ 8.19−7.24 (m, 15H, Ph), 6.74−6.72 (m, 1H, H^6), 5.26−5.18 (m, 2H, Cp′ and OCH_2), 5.10 (s, 1H, Cp′), 4.44−4.39 (m, 1H, OCH_2), 4.13 (d, 1H, J = 1.9 Hz, H^1 or H^4), 4.05−4.04 (m, 1H, H^1 or H^4), 3.48−3.45 (m, 2H, PCH_2), 1.41 (s, 9H, Bu^t), 1.09 (s, 3H, Cp′Me), −0.12 (ddd, 1H, J = 15.9, 9.6, 2.5 Hz, H^2 or H^3), −0.29 (dd, 1H, J = 16.8, 3.0 Hz, H^2 or H^3). ^{31}P NMR (160 MHz): δ 48.4. For minor product **9c-II**: ^{31}P NMR (160 MHz): δ 47.8.

[(η^5:η^1-2-Me-4-Bu^{t}C$_5$H$_2$CO$_2$CH$_2$CH$_2$PPh$_2$)Ru{η^4-CH$_2$=CHC(Me)=CHMe}][PF$_6$] (11c). IR (cm^{-1}, KBr): 1731 ($\nu_{C=O}$). HRMS calcd for $C_{31}H_{38}O_2PRu$ (M − PF_6^-) 575.1653, found *m*/*z* 575.1590. For major product **11c-I**: ^{1}H NMR (600 MHz): δ 8.14−7.39 (m, 10H, Ph), 5.87 (t, 1H, J = 8.5 Hz, H^6), 5.63 (s, 1H, Cp′), 5.25 (ddd, 1H, J = 22.8, 11.3, 7.7 Hz, OCH_2), 5.13 (dd, 1H, J = 3.0, 2.2 Hz, Cp′), 4.39 (ddt, 1H, J = 11.8, 5.2, 1.9 Hz, OCH_2), 3.70 (ddd, 1H, J = 8.0, 2.2, 1.4 Hz, H^4), 3.40−3.29 (m, 2H, PCH_2), 2.43 (s, 3H, Me), 2.24 (d, 3H, J = 1.4 Hz, Me), 1.58 (dd, 3H, J = 6.3, 1.2 Hz, Me), 1.35 (s, 9H, Bu^t), 0.20−0.17 (m, 1H, H^2 or H^3), −0.33 (ddd, 1H, J = 16.3, 9.3, 2.4 Hz, H^2 or H^3). ^{31}P NMR (160 MHz): δ 42.3. For minor product **11c-II**: ^{31}P NMR (160 MHz): δ 40.5.

Synthesis of [(η^5-2-Me-4-PhC$_5$H$_2$CO$_2$Et)Ru(PPh$_3$)(MeCN)$_2$][PF$_6$] (12). To a solution of [Cp′Ru(MeCN$_3$)][PF$_6$] (0.30 g, 0.5 mmol) in dichloromethane (20 mL) was added PPh_3 (0.13 g, 0.5 mmol), and the reaction mixture was stirred for 3 h at −78 °C. After the solvent was removed under reduced pressure, the residual solid was washed with ether several times and dried in vacuo. Yield: 99%. IR (cm^{-1}, KBr): 1711 ($\nu_{C=O}$). FAB MS: *m*/*z* 673 (M − PF_6^-). Anal. Calcd for $C_{37}H_{36}F_6N_2O_2P_2Ru$: C, 54.35; H, 4.44. Found: C, 54.12; H, 4.32. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46−7.13 (m, 20H, Ph), 5.27 (s, 1H, Cp′), 4.46 (s, 1H, Cp′), 4.13−4.05 (m, 1H, CH_2CH$_3$), 3.86−3.78 (m, 1H, CH_2CH$_3$), 2.31 (d, 3H, J = 1.0 Hz, Me), 2.15 (d, 3H, J = 1.2 Hz, Me), 1.90 (d, 3H, J = 1.2 Hz, Me), 1.10 (t, 3H, J = 7.1 Hz, CH$_2$CH_3). ^{31}P NMR (160 MHz): δ 46.3.

Reaction of [(η^5-2-Me-4-PhC$_5$H$_2$CO$_2$Et)Ru(PPh$_3$)(MeCN)$_2$][PF$_6$] (12) with Isoprene 2f. To a solution of ruthenium complex **12** (80 mg, 0.1 mmol) in dichloromethane (5 mL) was added isoprene **2f** (70 mg, 1.0 mmol), and the reaction mixture was refluxed for 12 h. The solvent was evaporated, and the residual oil was purified by chromatography on alumina using dichloromethane as eluent. After removal of the solvent, the residue was washed with ether several times and dried in vacuo. Yield: 83%. IR (cm^{-1}, KBr): 1722 ($\nu_{C=O}$). FAB MS: *m*/*z* 659 (M − PF_6^-). Anal. Calcd for $C_{38}H_{38}F_6O_2P_2Ru$: C, 56.79; H, 4.77. Found: C, 56.83; H, 4.65. For the major product: ^{1}H NMR (400 MHz): δ 7.77−7.46 (m, 20H, Ph), 5.67 (t, 1H, J = 8.3 Hz, H^5 or H^6), 5.52 (d, 1H, J = 2.0 Hz, Cp′), 5.10 (t, 1H, J = 2.2 Hz, Cp′), 4.05 (dq, 1H, J = 7.1, 3.6 Hz, CH_2CH$_3$), 3.85 (dq, 1H, J = 7.1, 3.6 Hz, CH_2CH$_3$), 3.38 (s, 1H, H^1 or H^4), 2.63 (d, 1H, J = 7.3 Hz, H^1 or H^4), 2.33 (s, 3H, Me), 2.15 (d, 3H, J = 1.7 Hz, Me), 1.18 (t, 3H, J = 7.1 Hz, CH$_2$CH_3), −0.10 to −0.25 (m, 2H, H^2 and H^3). ^{31}P NMR (160 MHz): δ 61.3. For the minor product: ^{1}H NMR (400 MHz): δ 7.77−7.46 (m, 20H, Ph), 5.81 (d, 1H, J = 2.2 Hz, Cp′), 4.84−4.80 (m, 2H, Cp′ and H^5 or H^6), 4.34 (q, 2H, J = 7.1 Hz, CH_2CH$_3$), 3.18 (s, 1H, H^1 or H^4), 2.90 (d, 1H, J = 6.8 Hz, H^1 or H^4), 2.51 (s, 3H, Me), 1.90 (d, 3H, J = 3.4 Hz, Me$_3$), 1.37 (t, 3H, J = 7.1 Hz, CH$_2$CH_3), −0.10 to −0.25 (m, 1H, H^2 or H^3), −0.45 (ddd, 1H, J = 11.7, 9.5, 2.2 Hz, H^2 or H^3). ^{31}P NMR (160 MHz): δ 62.5.

Table 2. Crystallographic Data for 6b-I·1.5Me$_2$CO

empirical formula	$C_{36.5}H_{41}F_6O_{3.5}P_2Ru$
fw	812.73
cryst color, habit	yellow, prismatic
cryst dimens	0.40 × 0.30 × 0.20 mm
cryst syst	triclinic
lattice params	a = 12.548(3) Å
	b = 14.590(3) Å
	c = 11.140(2) Å
	α = 107.23(1)°
	β = 111.85(1)°
	γ = 70.55(2)°
	V = 1750.1(7) Å^3
space proup	$P\bar{1}$ (#2)
Z value	2
D_{calcd}	1.542 g cm^{-3}
F(000)	832
μ(Mo Kα)	6.09 cm^{-1}
no. reflns measd	
total	8423
unique	8055 (R_{int} = 0.105)
absorp corr	ψ-scan
p-factor	0.1770
no. observations	7370 ($I > 3.0\sigma(I)$)
no. params	451
refln/param ratio	16.34
residuals: R; R_w	0.064; 0.105
goodness of fit indicator	1.15

X-ray Diffraction Analysis. Crystals of complex **6b-I** suitable for X-ray diffraction were obtained by recrystallization from acetone. The ^{1}H NMR spectrum of the crystals suggested that the crystals consisted of the major isomer of **6b**. All measurements were performed on a Rigaku AFC7R automated four-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at −50 °C in the range 6° < 2θ < 55° with a scan rate 16° of min^{-1}. Intensities were measured by the 2θ−ω scan method. Three standard reflections were monitored at every 150 measurements as a check of the stability of the crystals, and no damage was observed in all measurements. Intensities were corrected for Lorentz and

polarization effects. Absorption correction was made with the ψ-scan technique. The structures were solved by Patterson methods and refined by full-matrix least squares using anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were located at the calculated positions with a distance of 0.95 Å. In the preliminary communication,[14] we made a mistake in the refinement of one of the solvate molecules. The solvate molecule is located close to the symmetric center and has been refined as two disordered models with an occupancy of 0.5. A summary of the crystallographic data is given in Table 2.

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Supporting Information Available: Details of crystallographic work (CIF file). This material is available free of charge via the Internet at http://pubs.acs.org. The data have also been deposited at the Cambridge Crystallographic Data Center (No. CCDC-158104).

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