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

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The treatment of planar-chiral ($\eta^{5:\eta^{1}}$ -cyclopentadienylphosphine)bis(acetonitrile)ruthenium complexes 1 with prochiral dienes led to the ligand-exchange reaction that gave $(\eta^5; \eta^1)$ 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 1,3diene complexes are good chiral synthons for preparing natural products.⁵ Although it has been reported that

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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 planarchiral cyclopentadienylruthenium (Cp'Ru) complexes.⁸ One of our first efforts was to examine enantiofaceselective 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 planarchiral 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 reactions¹¹ 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, PR₃)

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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.



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 ¹H 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 (H¹, H⁴) and *anti*-protons (H², H³) 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 H₂C=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-2,4hexadiene 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-penta-









 Table 1. Reaction of Ruthenium Complexes 1 with Prochiral Dienes

entry	substrate	diene	product	yield/% ^a	$\mathrm{de}/\%^{b,c}$
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	2ĥ	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	2ĸ	11b	85	38 (I)
16	$\mathbf{1c} (\mathbf{R} = \mathbf{Bu}^t)$	2d	4 c	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 ³¹P NMR. ^c The structure of the major product is given in parentheses; see Chart 5.

diene **2d** gave a diastereomeric mixture of η^4 -diene complex 4a in 93% yield (entry 1). The ¹H and ³¹P 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-1,3butadiene **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

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(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 $Cp(\eta^4$ -diene)-RuL complexes.¹⁷ The ¹H 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 (H¹ and H⁴) 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 antiproton 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 ¹H 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-1.5Me₂CO. Hydrogen atoms, PF_6^- counteranion, and Me₂CO 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 ¹H NMR spectra of complex **5** are similar to those of **4**, the major product should adopt a conformation of **5-I**.



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 ¹H 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- π 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 methvlene 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 planarchiral 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. ¹H, ¹³C, and ³¹P 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 SiMe₄ as the internal standard for ¹H and ¹³C NMR, and 85% H₃PO₄ as the external standard for ³¹P 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.

[(η⁵:η¹-2,4-Me₂C₅H₂CO₂CH₂CH₂PPh₂)Ru{η⁴-CH₂=C(Me)-C(Me)=CH₂]][PF₆] (3a). Yield: 86%. ¹H 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 OCH₂), 4.43–4.35 (m, 1H, OCH₂), 3.46–3.34 (m, 2H, PCH₂), 3.31 (s, 1H, H¹ or H⁴), 3.19 (s, 1H, H¹ or H⁴), 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, H² or H³), -0.58 (dd, 1H, J = 17.6, 2.0, Hz, H² or H³). IR (cm⁻¹, KBr): 1721 (ν_{C=0}). FAB MS: *m/z* 533 (M – PF₆⁻). Anal. Calcd for C₂₈H₃₂F₆O₂P₂Ru: C, 49.63; H, 4.76. Found: C, 49.40; H, 4.50.

 $[(\eta^{5}:\eta^{1}-2,4-\text{Me}_{2}\text{C}_{5}\text{H}_{2}\text{CO}_{2}\text{CH}_{2}\text{CH}_{2}\text{PPh}_{2})\text{Ru}(\eta^{4}-\text{CH}_{2}=\text{CHCH}=$ CHMe)][PF₆] (4a). IR (cm⁻¹, KBr): 1731 (v_{C=0}). 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**: ¹H 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, OCH₂), 5.14-5.12 (m, 1H, Cp'), 4.48-4.41 (m, 1H, OCH₂), 3.43-3.24 (m, 2H, PCH₂), 3.11 (d, 1H, J = 8.1 Hz, H⁴), 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, H² or H³), -0.22 to -0.28 (m, 1H, H² or H³). ³¹P NMR (160 MHz): δ 50.2. For minor product 4a-II: ¹H 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, H⁵ or H⁶), 5.55 (m, 1H, H⁵ or H⁶), 5.43-5.41 (m, 1H, Cp'), 5.31-5.18 (m, 1H, OCH₂), 4.34-4.29 (m, 1H, OCH₂), 3.57-3.53 (m, 1H, PCH₂), 3.43-3.24 (m, 1H, PCH₂), 3.04 (d, 1H, J = 6.3 Hz, H¹), 2.18 (d, 3H, J = 1.7Hz, 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, H² or H³), 0.19-0.13 (m, 1H, H² or H³). ³¹P NMR (160 MHz): δ 48.4.

 $[(\eta^5:\eta^1-2,4-Me_2C_5H_2CO_2CH_2CH_2PPh_2)Ru(\eta^4-CH_2=CHCH=$ **CHEt**)][**PF**₆] (5a). IR (cm⁻¹, KBr): 1728 ($\nu_{C=0}$). FAB MS: m/z533 (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: ¹H NMR (400 MHz): δ 8.03–7.45 (m, 10H, Ph), 6.01–5.98 (m, 1H, H⁵ or H⁶), 5.80 (dd, 1H, J = 9.5, 5.1 Hz, H⁵ or H⁶), 5.76 (s, 1H, Cp'), 5.30-5.15 (m, 1H, OCH₂), 5.14-5.13 (m, 1H, Cp'), 4.44-4.39 (m, 1H, OCH2), 3.52-3.27 (m, 2H, PCH2), 3.14 (d, 1H, J = 7.8 Hz, H⁴), 2.31 (d, 3H, J = 1.7 Hz, Cp'Me), 2.08 (s, 3H, Cp'Me), 1.73-1.65 (m, 1H, CH₂CH₃), 1.05 (t, 3H, J = 7.3 Hz, CH_2CH_3), 0.56-0.48 (m, 1H, H² or H³), -0.17 to -0.23 (m, 1H, H² or H³). ³¹P NMR (160 MHz): δ 49.9. For minor product **5a-II**: ¹H NMR (400 MHz): δ 8.03-7.45 (m, 10H, Ph), 6.07-6.05 (m, 1H, H⁵ or H⁶), 5.74 (s, 1H, Cp'), 5.55 (m, 1H, H⁵ or H⁶), 5.43-5.42 (m, 1H, Cp'), 5.30-5.15 (m, 1H, OCH₂), 4.36-4.29 (m, 1H, OCH2), 3.52-3.27 (m, 2H, PCH2), 3.04 (d, 1H, J = 7.1 Hz, H¹), 2.17 (s, 3H, Cp'*Me*), 2.16 (d, 3H, J = 1.7Hz, Cp'*Me*), 1.73-1.65 (m, 1H, CH₂CH₃), 0.86 (t, 3H, J = 7.3Hz, CH₂CH₃), 0.27-0.16 (m, 2H, H² and H³). ³¹P NMR (160 MHz): δ 48.5.

 $[(\eta^{5}:\eta^{1}-2,4-Me_{2}C_{5}H_{2}CO_{2}CH_{2}CH_{2}PPh_{2})Ru\{\eta^{4}-CH_{2}=CHC (Me)=CH_2$][PF₆] (6a). IR (cm⁻¹, KBr): 1727 ($\nu_{C=0}$). 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**: ¹H 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, H⁶), 5.91 (s, 1H, Cp'), 5.55–5.43 (m, 2H, Cp' and OCH2), 4.70-4.62 (m, 1H, OCH2), 3.76-3.66 (m, 2H, PCH2), 3.55 (s, 1H, H¹ or H⁴), 3.49-3.46 (m, 1H, H¹ or H⁴), 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, H² and H³). ¹³C NMR (150 MHz): δ 166.5 (C=O), 134.2-129.1 (Ph), 117.6, 110.1, 105.4, 93.9 (J = 5.0Hz), 87.6, 87.5, 82.5, 59.6 (J = 5.8 Hz, OCH₂), 53.8 (C¹ or C⁴), 52.2 (C¹ or C⁴), 23.3 (PCH₂), 23.0 (Me on diene), 12.1 (Cp'Me), 11.5 (Cp'*Me*). ³¹P NMR (160 MHz): δ 52.2. For minor product **6a-II**: ³¹P NMR (160 MHz): δ 51.9.

[(η⁵:η¹⁻²,4-Me₂C₅H₂CO₂CH₂CH₂PPh₂)Ru(η⁴-CH₂=CHCH= CHPh)][PF₆] (8a). IR (cm⁻¹, KBr): 1734 (ν_{C=0}). FAB MS: *m/z* 581 (M – PF₆⁻). Anal. Calcd for C₃₂H₃₂F₆O₂P₂Ru: C, 52.97; H, 4.45. Found: C, 52.69; H, 4.45. For major product 8a-II: ¹H NMR (600 MHz): δ 7.69–7.23 (m, 15H, Ph), 6.82 (dd, 1H, J = 6.0, 10.7 Hz, H⁵ or H⁶), 5.87 (s, 1H, Cp'), 5.68–5.64 (m, 1H, H⁵ or H⁶), 5.16 (q, 1H, J = 1.6 Hz, Cp'), 5.14–5.07 (m, 1H, OCH₂), 4.42–4.37 (m, 1H, OCH₂), 3.46–3.31 (m, 3H, PCH₂ and H¹), 2.13 (d, 3H, J = 1.6 Hz, Cp'*Me*), 1.60 (s, 3H, Cp'*Me*), 1.56 (t, 1H, J = 10.7 Hz, H² or H³), 0.81 (dd, 1H, J = 15.1, 10.2 Hz, H² or H³). ³¹P NMR (160 MHz): δ 47.4.

[(η^{5} : η^{1} -2,4-Me₂C₅H₂CO₂CH₂CH₂PPh₂)Ru{ η^{4} -CH₂=CHC-(Ph)=CH₂}][PF₆] (9a). IR (cm⁻¹, KBr): 1733 ($\nu_{C=0}$). FAB MS: *m*/*z* 581 (M – PF₆⁻). Anal. Calcd for C₃₂H₃₂F₆O₂P₂Ru: C, 52.97; H, 4.45. Found: C, 52.48; H, 4.18. For major product 9a-I: ¹H NMR (600 MHz): δ 8.13–7.44 (m, 15H, Ph), 6.73 (t, 1H, *J* = 8.5 Hz, H⁶), 5.24–5.13 (m, 3H, Cp' and OCH₂), 4.44 (ddd, 1H, *J* = 11.5, 5.5, 2.2 Hz, OCH₂), 4.20 (s, 1H, H¹ or H⁴), 3.53–3.37 (m, 3H, PCH₂ and H¹ or H⁴), 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, H² or H³), -0.32 (dd, 1H, *J* = 16.2, 2.5 Hz, H² or H³). ³¹P NMR (160 MHz): δ 51.5.

[($\eta^{5:}\eta^{1.2}$, **4**-**Me**₂**C**₅**H**₂**CO**₂**CH**₂**CH**₂**PPh**₂)**Ru**{ η^{4-} **CH**₂**=C**(**Me**)-**CH=CHMe**}][**PF**₆] (**10a**). IR (cm⁻¹, KBr): 1725 ($\nu_{C=0}$). FAB MS: m/z 533 (M – PF₆⁻). Anal. Calcd for C₂₈H₃₂F₆O₂P₂Ru: C, 49.63; H, 4.76. Found: C, 49.41; H, 4.51. For major product **10a-I**: ¹H NMR (600 MHz): δ 8.03–7.42 (m, 10H, Ph), 5.66 (d, 1H, J = 9.3 Hz, H⁵), 5.35 (s, 1H, Cp'), 5.23 (ddd, 1H, J = 11.5, 11.5, 8.0 Hz, OCH₂), 5.12 (s, 1H, Cp'), 4.45 (ddt, 1H, J = 11.5, 5.2, 1.9 Hz, OCH₂), 3.36 (dt, 1H, J = 1.4 Hz, H⁴), 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, H² or H³), -0.46 (dd, 1H, J = 16.2, 1.9 Hz, H² or H³). ³¹P NMR (160 MHz): δ 49.5.

 $[(\eta^{5}:\eta^{1}-2,4-Me_{2}C_{5}H_{2}CO_{2}CH_{2}CH_{2}PPh_{2})Ru\{\eta^{4}-CH_{2}=CHC-$ (Me)=CHMe}] [PF₆] (11a). IR (cm⁻¹, KBr): 1731 ($\nu_{C=0}$). FAB MS: m/z 533 (M - PF₆⁻). Anal. Calcd for C₂₈H₃₂F₆O₂P₂Ru: C, 49.63; H, 4.76. Found: C, 49.35; H, 4.80. For major product 11a-I: ¹H NMR (600 MHz): δ 7.92–7.42 (m, 10H, Ph), 5.78 (t, 1H, J = 8.3 Hz, H⁶), 5.59 (s, 1H, Cp'), 5.23 (ddd, 1H, J =22.5, 11.5, 7.6 Hz, OCH₂), 5.04 (s, 1H, Cp'), 4.40 (ddt, 1H, J= 11.5, 5.2, 1.9 Hz, OCH₂), 3.49–3.24 (m, 2H, PCH₂), 3.06 (d, 1H, J = 8.3 Hz, H⁴), 2.42 (s, 3H, CH₃), 2.21 (s, 3H, CH₃), 2.06 (s, 3H, CH₃), 1.56 (dd, 3H, J = 6.3, 1.4 Hz, CH₃), 0.23 (dq, 1H, J = 21.7, 6.3 Hz, H² or H³), -0.25 (ddd, 1H, J = 15.9, 9.9, 2.2Hz, H² or H³). ³¹P NMR (160 MHz): δ 51.3. For minor product **11a-II**: ¹H NMR (400 MHz): δ 7.92–7.42 (m, 10H, Ph), 5.52 (t, 1H, J = 8.3 Hz, H⁵), 5.35 (s, 1H, Cp'), 5.31 (s, 1H, Cp'), 5.15 (ddd, 1H, J = 23.3, 11.5, 7.6 Hz, OCH₂), 4.32 (ddt, 1H, J =11.5, 4.9, 2.2 Hz, OCH2), 3.49-3.24 (m, 2H, PCH2), 2.93 (dd, 1H, J = 8.3, 1.9 Hz, H¹), 2.42 (s, 3H, CH₃), 2.21 (s, 3H, CH₃), 2.14 (s, 3H, CH₃), 1.52 (dd, 3H, J = 6.3, 1.6 Hz, CH₃), 0.07 (ddd, 1H, J = 15.4, 9.3, 2.2 Hz, H² or H³), 0.01 (dq, 1H, J = 21.2, 6.3 Hz, H² or H³). ³¹P NMR (160 MHz): δ 49.2.

 $[(\eta^{5}:\eta^{1}-2-Me-4-PhC_{5}H_{2}CO_{2}CH_{2}CH_{2}PPh_{2})Ru(\eta^{4}-CH_{2}=$ CHCH=CHMe)][PF₆] (4b). IR (cm⁻¹, KBr): 1732 (v_{C=0}). 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**: ¹H NMR (400 MHz): δ 7.90–7.40 (m, 15H, Ph), 6.46 (s, 1H, Cp'), 6.14-6.09 (m, 1H, H⁵ or H⁶), 5.88 (dd, 1H, J = 10.3, 5.6 Hz, H⁵ or H⁶), 5.76 (dd, 1H, J = 4.2, 2.4 Hz, Cp'), 5.37-5.19 (m, 1H, OCH₂), 4.54 (dq, 1H, J = 4.2, 2.4 Hz, OCH₂), 3.46-3.24 (m, 2H, PCH₂), 2.79 (s, 1H, H⁴), 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, H² or H³), -0.26 (dd, 1H, J = 12.2, 11.0 Hz, H² or H³). ³¹P NMR (160 MHz): δ 50.8. For minor product **4b-II**: ¹H 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, H⁵ or H⁶), 5.73–5.69 (m, 1H, H⁵ or H⁶), 5.37– 5.19 (m, 1H, OCH₂), 4.45 (dt, 1H, J = 5.4, 2.0 Hz, OCH₂), 3.46-3.24 (m, 2H, PCH₂), 3.05 (d, 1H, J = 6.8 Hz, H¹), 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, H² or H³), -0.12 (dd, 1H, J = 10.5, 12.4 Hz, H² or H³). ³¹P NMR (160 MHz): δ 49.3.

 $[(\eta^5:\eta^1-2-Me-4-PhC_5H_2CO_2CH_2CH_2PPh_2)Ru(\eta^4-CH_2=$ CHCH=CHEt)][PF₆] (5b). IR (cm⁻¹, KBr): 1733 (v_{C=0}). 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**: ¹H NMR (400 MHz): δ 7.89–7.41 (m, 15H, Ph), 6.45 (s, 1H, Cp'), 6.12-6.06 (m, 1H, H⁵ or H⁶), 5.88 (dd, 1H, J = 9.8, 5.4 Hz, H⁵ or H⁶), 5.76 (dd, 1H, J = 3.9, 2.4 Hz, Cp'), 5.35-5.19 (m, 1H, OCH₂), 4.53 (ddt, 1H, J = 9.3, 5.1, 2.2 Hz, OCH₂), 3.47-3.29 (m, 2H, PCH₂), 3.05 (d, 1H, J = 8.1 Hz, H¹), 2.44(d, 3H, J = 1.7 Hz, Cp'Me), 1.76 - 1.68 (m, 1H, CH₂CH₃), 1.13 - 1.051.05 (m, 3H, CH₂CH₃), 0.26-0.22 (m, 1H, H² or H³), -0.18 to -0.22 (m, 1H, H² or H³). ³¹P NMR (160 MHz): δ 50.6. Minor product **5b-II**: ¹H 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, H⁵ or H⁶), 5.73-5.69 (m, 1H, H⁵ or H⁶), 5.35–5.19 (m, 1H, OCH₂), 4.39 (ddt, 1H, J = 9.5, 5.1, 2.2 Hz, OCH_2), 3.47–3.29 (m, 3H, PCH₂, H¹), 2.27 (d, 3H, J = 1.7 Hz, Cp'Me), 1.29-1.26 (m, 2H, CH₂CH₃), 0.65-0.53 (m, 4H, $CH_2C\mathit{H}_3$ 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.

 $[(\eta^{5}:\eta^{1}-2-\text{Me}-4-\text{PhC}_{5}\text{H}_{2}\text{CO}_{2}\text{CH}_{2}\text{CH}_{2}\text{PPh}_{2})\text{Ru}\{\eta^{4}-\text{CH}_{2}=$ **CHC(Me)=CH₂**][**PF**₆] (6b). IR (cm⁻¹, KBr): 1727 ($\nu_{C=0}$). FAB MS: m/z 581 (M - PF₆⁻). Anal. Calcd for C₃₂H₃₂F₆O₂-P₂Ru: C, 52.97; H, 4.45. Found: C, 52.74; H, 4.25. For major product **6b-I**: ¹H 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 = 1.0Hz, Cp'), 5.82-5.76 (m, 2H, H⁶ and Cp'), 5.33-5.22 (m, 1H, OCH₂), 4.49 (ddt, 1H, J = 11.7, 5.6, 2.2 Hz, OCH₂), 3.53-3.36 (m, 3H, PCH₂ and H¹ or H⁴), 3.32 (s, 1H, H¹ or H⁴), 2.58 (s, 3H, CH₃), 2.30 (d, 3H, J = 1.5 Hz, CH₃), -0.17 (dd, 1H, J =16.1, 2.0 Hz, H² or H³), -0.29 (ddd, 1H, J = 15.9, 9.5, 2.2 Hz, H² or H³). ¹³C 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, OCH₂), 53.5 (J = 4.1 Hz, C¹ or C⁴), 53.3 (J =4.1 Hz, C¹ or C⁴), 23.2 (PCH₂), 22.9 (Me on diene), 11.65 (Cp'*Me*). ³¹P NMR (160 MHz): δ 53.0. For minor product **6b**-**II**: ³¹P NMR (160 MHz): δ 51.5.

[$(\eta^{5}:\eta^{1}-2-Me-4-PhC_{5}H_{2}CO_{2}CH_{2}CH_{2}PPh_{2})Ru(\eta^{4}-CH_{2}=$ CHCH=CHPh)][PF₆] (8b). IR (cm⁻¹, KBr): 1731 ($\nu_{C=0}$). HRMS calcd for C₃₇H₃₄O₂PRu (M – PF₆⁻) 643.1340, found *m/z* 643.1332. ¹H 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, H⁵ or H⁶), 6.40 (d, 2H, *J* = 7.4 Hz, Ph), 5.81–5.76 (m, 2H, Cp' and H⁵ or H⁶), 5.13 (ddd, 1H, *J* = 23.9, 12.4, 7.4 Hz, OCH₂), 4.39 (ddt, 1H, *J* = 11.8, 5.0, 2.5 Hz, OCH₂), 3.41–3.34 (m, 1H, PCH₂), 3.28–3.22 (m, 2H, PCH₂ and H¹), 2.21 (d, 3H, J = 1.4 Hz, Cp'*Me*), 1.40 (t, 1H, J = 11.0 Hz, H² or H³), 0.62–0.58 (m, 1H, H² or H³). ³¹P NMR (160 MHz): δ 45.3.

[($\eta^{5}:\eta^{1}-2$ -Me-4-PhC₅H₂CO₂CH₂CH₂PPh₂)Ru{ η^{4} -CH₂= CHC(Ph)=CH₂}][PF₆] (9b). IR (cm⁻¹, KBr): 1738 ($\nu_{C=0}$). HRMS calcd for C₃₇H₃₄O₂PRu (M – PF₆⁻) 643.1340, found *m*/*z* 643.1360. For major product 9b-I: ¹H NMR (600 MHz): δ 8.25–7.38 (m, 20H, Ph), 6.71 (t, 1H, J = 9.3 Hz, H⁶), 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, OCH₂), 4.52 (ddt, 1H, J = 11.5, 5.2, 2.2 Hz, OCH₂), 4.22 (s, 1H, H¹ or H⁴), 3.57–3.45 (m, 2H, PCH₂), 2.61 (ddd, 1H, J = 8.0, 2.2, 1.4 Hz, H¹ or H⁴), 1.09 (d, 3H, J = 1.7Hz, CH₃), -0.08 (ddd, 1H, J = 15.1, 9.3, 2.2 Hz, H² or H³), -0.21 (dd, 1H, J = 16.8, 2.7 Hz, H² or H³). ³¹P NMR (160 MHz): δ 53.0. For minor product 9b-II: ³¹P NMR (160 MHz): δ 51.8.

 $[(\eta^{5}:\eta^{1}-2-Me-4-PhC_{5}H_{2}CO_{2}CH_{2}CH_{2}PPh_{2})Ru\{\eta^{4}-CH_{2}=$ **C(Me)CH=CHMe**][**PF**₆] (10b). IR (cm⁻¹, KBr): 1733 ($\nu_{C=0}$). HRMS calcd for $C_{33}H_{34}O_2PRu$ (M – PF₆⁻) 595.1340, found m/z595.1339. For major product: **10b-I**: ¹H 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, H⁵), 5.29 (ddd, 1H, J = 22.7, 11.7, 7.1 Hz, OCH₂), 4.55 (ddt, 1H, J = 11.7, 5.1, 2.2Hz, OCH₂), 3.46-3.25 (m, 2H, PCH₂), 2.74 (s, 1H, H⁴), 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, H² or H³), -0.44 (dd, 1H, J = 16.6, 2.2 Hz, H² or H³). ³¹P NMR (160 MHz): δ 50.7. For minor product 10b-II: 1H NMR (400 MHz): 8 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, H⁶), 5.22–5.17 (m, 1H, OCH₂), 4.40–4.32 (m, 1H, OCH₂), 3.46-3.25 (m, 2H, PCH₂), 3.11 (s, 1H, H¹), 2.58 (s, 3H, CH₃), 2.28 (d, 3H, J = 1.5 Hz, CH₃), 0.72 (dd, 3H, J =6.1, 1.7 Hz, CH₃), 0.22-0.14 (m, 1H, H² or H³), -0.10 to -0.14(m, 1H, H² or H³). ³¹P NMR (160 MHz): δ 50.4.

 $[(\eta^{5}:\eta^{1}-2-\text{Me-4-PhC}_{5}H_{2}CO_{2}CH_{2}CH_{2}PPh_{2})Ru\{\eta^{4}-CH_{2}=$ **CHC(Me)=CHMe**][**PF**₆] (11b). IR (cm⁻¹, KBr): 1731 ($\nu_{C=0}$). HRMS calcd for $C_{33}H_{34}O_2PRu$ (M – PF₆⁻) 595.1340, found m/z595.1339. For major product 11b-I: ^1H NMR (400 MHz): δ 7.88-7.39 (m, 15H, Ph), 6.29 (s, 1H, Cp'), 5.80 (t, 1H, J = 8.5 Hz, H⁶), 5.66 (dd, 1H, J = 4.1, 2.4 Hz, Cp'), 5.29 (ddd, 1H, J = 22.7, 11.7, 7.3 Hz, OCH₂), 4.50 (ddt, 1H, J = 11.7, 5.1, 3.5 Hz, OCH₂), 3.49-3.30 (m, 2H, PCH₂), 2.55 (s, 3H, Me), 2.33 (d, 3H, J = 1.7 Hz, Me), 2.15 (d, 1H, J = 8.1 Hz, H⁴), 1.57 (dd, 3H, J = 6.3, 1.5 Hz, Me), 0.34–0.25 (m, 1H, H² or H³), -0.26 (ddd, 1H, J = 15.9, 9.8, 2.2 Hz, H² or H³). ³¹P NMR (160 MHz): δ 51.8. For minor product **11b-II**: ¹H 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, H⁵), 5.21– 5.18 (m, 1H, OCH₂), 4.43-4.38 (m, 1H, OCH₂), 3.49-3.30 (m, 2H, PCH₂), 2.99 (d, 1H, J = 7.5 Hz, H¹), 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, H² and H³). ³¹P NMR (160 MHz): δ 49.3.

 $[(\eta^{5}:\eta^{1}-2-\text{Me-4-Bu}^{t}C_{5}H_{2}CO_{2}CH_{2}CH_{2}PPh_{2})Ru(\eta^{4}-CH_{2}=$ **CHCH=CHMe)][PF₆] (4c).** IR (cm⁻¹, KBr): 1731 ($\nu_{C=0}$). 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: ¹H 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, H⁵ or H⁶), 5.85 (s, 1H, Cp'), 5.74 (dd, 1H, *J* = 9.8, 5.4 Hz, H⁵ or H⁶), 5.33-5.22 (m, 2H, CpH, OCH2), 4.44-4.40 (m, 1H, OCH2), 3.71 (d, 1H, J = 7.8 Hz, H⁴), 3.42–3.24 (m, 2H, PCH₂), 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, H² or H³), -0.29 to -0.35(m, 1H, H² or H³). ³¹P NMR (160 MHz): δ 46.3. For minor product **4c-II**: ¹H 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, H⁵ or H⁶), 5.83 (s, 1H, Cp'), 5.55 (t, 1H, J = 2.4 Hz, Cp'), 5.33-5.22 (m, 2H, H⁵ or H⁶ and OCH₂), 4.44–4.40 (m, 1H, OCH₂), 3.42-3.24 (m, 2H, PCH₂), 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, H² or H³), 0.16–0.10 (m, 1H, H² or H³). ³¹P NMR (160 MHz): δ 46.1.

 $[(\eta^5:\eta^1-2-\text{Me-4-Bu}^t\text{C}_5\text{H}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{PPh}_2)\text{Ru}(\eta^4-\text{CH}_2=$ **CHCH=CHEt)** [**PF**₆] (5c). IR (cm⁻¹, KBr): 1733 ($\nu_{C=0}$). FAB MS: m/z 575 (M - PF₆⁻). Anal. Calcd for C₃₁H₃₈F₆O₂P₂Ru: C, 51.74; H, 5.32. Found: C, 51.50; H, 5.08. For major product 5c-I: ¹H NMR (400 MHz): δ 8.18–8.13 (m, 2H, Ph), 7.78– 7.42 (m, 8H, Ph), 6.12-6.08 (m, 1H, H⁵ or H⁶), 5.83 (s, 1H, Cp'), 5.73 (dd, 1H, J = 9.5, 5.1 Hz, H⁵ or H⁶), 5.32-5.22 (m, 2H, Cp' and OCH₂), 4.45-4.38 (m, 1H, OCH₂), 3.74 (d, 1H, J = 7.8 Hz, H⁴), 3.52–3.29 (m, 2H, PCH₂), 2.32 (d, 3H, J = 1.7Hz, Cp'Me), 1.82-1.70 (m, 2H, CH₂CH₃), 1.34 (s, 9H, Bu⁴), 1.05 (t, 3H, J = 7.3 Hz, CH_2CH_3), 0.50–0.40 (m, 1H, H² or H³), -0.23 to -0.30 (m, 1H, H² or H³). ³¹P NMR (160 MHz): δ 46.0. For minor product 5c-II: ¹H NMR (400 MHz): δ 8.18–8.13 (m, 2H, Ph), 7.78-7.42 (m, 8H, Ph), 6.12-6.08 (m, 1H, H⁵ or H⁶), 5.80 (s, 1H, Cp'), 5.55-5.53 (m, 2H, Cp' and H⁵ or H⁶), 5.16-5.12 (m, 1H, OCH₂), 4.26-4.18 (m, 1H, OCH₂), 3.52-3.29 (m, 2H, PCH₂), 2.97 (d, 1H, J = 5.9 Hz, H¹), 2.12 (d, 3H, J = 1.5 Hz, Cp'Me), 1.82-1.70 (m, 2H, CH₂CH₃), 1.40 (s, 9H, Bu^t), 0.84 (t, 3H, J = 7.3 Hz, CH₂CH₃), 0.32–0.30 (m, 1H, H² or H³), 0.17–0.14 (m, 1H, H² or H³). ³¹P NMR (160 MHz): δ 46.2.

 $[(\eta^{5}:\eta^{1}-2-\text{Me-4-Bu}^{t}C_{5}H_{2}CO_{2}CH_{2}CH_{2}PPh_{2})Ru\{\eta^{4}-CH_{2}=$ **CHC(Me)=CH₂}][PF₆] (6c).** IR (cm⁻¹, KBr): 1733 (v_{C=0}). 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: ¹H 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, H⁶), 5.67 (s, 1H, Cp'), 5.28-5.17 (m, 2H, Cp' and OCH₂), 4.41-4.33 (m, 1H, OCH₂), 3.81-3.78 (m, 1H, H¹ or H⁴), 3.43-3.38 (m, 2H, PCH₂), 3.21 (s, 1H, H¹ or H⁴), 2.47 (d, 3H, J = 0.7 Hz, CH₃), 2.21 (d, 3H, J = 1.5 Hz, CH₃), 1.37 (s, 9H, Bu⁴), -0.18- -0.23 (m, 1H, H² or H³), -0.30 to -0.37 (m, 1H, H² or H³). ¹³C 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 (CMe_3), 31.4 (CMe_3), 23.4 (d, J =31 Hz, PCH2), 23.2 (Me), 12.0 (Me). $^{31}\mathrm{P}$ NMR (160 MHz): δ 48.8. For minor product 6c-II: ³¹P NMR (160 MHz): δ 47.4.

[($\eta^{5}:\eta^{1}$ -2-Me-4-Bu⁴C₅H₂CO₂CH₂CH₂PPh₂)Ru{ η^{4} -CH₂= CHC(Ph)=CH₂}][PF₆] (9c). IR (cm⁻¹, KBr): 1735 ($\nu_{C=0}$). HRMS calcd for C₃₅H₃₈O₂PRu (M – PF₆⁻) 623.1653, found *m*/*z* 623.1645. For major product 9c-I: ¹H NMR (400 MHz): δ 8.19–7.24 (m, 15H, Ph), 6.74–6.72 (m, 1H, H⁶), 5.26–5.18 (m, 2H, Cp' and OCH₂), 5.10 (s, 1H, Cp'), 4.44–4.39 (m, 1H, OCH₂), 4.13 (d, 1H, *J* = 1.9 Hz, H¹ or H⁴), 4.05–4.04 (m, 1H, H¹ or H⁴), 3.48–3.45 (m, 2H, PCH₂), 1.41 (s, 9H, Bu'), 1.09 (s, 3H, Cp'Me), -0.12 (ddd, 1H, *J* = 15.9, 9.6, 2.5 Hz, H² or H³), -0.29 (dd, 1H, *J* = 16.8, 3.0 Hz, H² or H³). ³¹P NMR (160 MHz): δ 48.4. For minor product 9c-II: ³¹P NMR (160 MHz): δ 47.8.

[(η^{5} : η^{1} -2-Me-4-Bu'C₅H₂CO₂CH₂CH₂PPh₂)Ru{ η^{4} -CH₂= CHC(Me)=CHMe}][PF₆] (11c). IR (cm⁻¹, KBr): 1731 ($\nu_{C=0}$). HRMS calcd for C₃₁H₃₈O₂PRu (M – PF₆⁻) 575.1653, found *m/z* 575.1590. For major product 11c-I: ¹H NMR (600 MHz): δ 8.14–7.39 (m, 10H, Ph), 5.87 (t, 1H, J = 8.5 Hz, H⁶), 5.63 (s, 1H, Cp'), 5.25 (ddd, 1H, J = 22.8, 11.3, 7.7 Hz, OCH₂), 5.13 (dd, 1H, J = 3.0, 2.2 Hz, Cp'), 4.39 (ddt, 1H, J = 11.8, 5.2, 1.9 Hz, OCH₂), 3.70 (ddd, 1H, J = 8.0, 2.2, 1.4 Hz, H⁴), 3.40–3.29 (m, 2H, PCH₂), 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'), 0.20– 0.17 (m, 1H, H² or H³), -0.33 (ddd, 1H, J = 16.3, 9.3, 2.4 Hz, H² or H³). ³¹P NMR (160 MHz): δ 42.3. For minor product 11c-II: ³¹P NMR (160 MHz): δ 40.5.

Synthesis of $[(\eta^5-2-\text{Me-4-PhC}_5\text{H}_2\text{CO}_2\text{Et})\text{Ru}(\text{PPh}_3)-(\text{MeCN})_2][\text{PF}_6]$ (12). To a solution of $[\text{Cp'Ru}(\text{MeCN}_3)][\text{PF}_6]$ (0.30 g, 0.5 mmol) in dichloromethane (20 mL) was added PPh₃ (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

Table 2. Crystallographic Data for 6b-I-1.5Me₂CO

abie 2. Crystanograph	
empirical formula	$C_{36.5}H_{41}F_6O_{3.5}P_2Ru$ 812 73
orrest color babit	vellow prismatic
ci yst color, habit	$0.40 \times 0.20 \times 0.20$
cryst dimens	$0.40 \times 0.30 \times 0.20$ IIIII
cryst syst	
lattice params	a = 12.548(3) A
	b = 14.590(3) A
	c = 11.140(2) A
	$\alpha = 107.23(1)^{\circ}$
	$\beta = 111.85(1)^{\circ}$
	$\gamma = 70.55(2)^{\circ}$
	$V = 1750.1(7) \text{ Å}^3$
space proup	$P\overline{1}$ (#2)
Żvalue	2
$D_{ m calcd}$	1.542 g cm^{-3}
F(000)	832
μ(Μο Κα)	6.09 cm^{-1}
no. reflns measd	
total	8423
unique	$8055 \ (R_{\rm int} = 0.105)$
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
0	

 $(ν_{C=0})$. FAB MS: *m/z* 673 (M − PF₆⁻). Anal. Calcd for C₃₇H₃₆F₆N₂O₂P₂Ru: C, 54.35; H, 4.44. Found: C, 54.12; H, 4.32. ¹H NMR (CDCl₃, 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, CH₂CH₃), 3.86−3.78 (m, 1H, CH₂CH₃), 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, CH₂CH₃). ³¹P NMR (160 MHz): δ 46.3.

Reaction of $[(\eta^5-2-Me-4-PhC_5H_2CO_2Et)Ru(PPh_3)-$ (MeCN)2][PF6] (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 ($\nu_{C=0}$). FAB MS: m/z 659 (M - PF₆⁻). Anal. Calcd for C₃₈H₃₈F₆O₂P₂Ru: C, 56.79; H, 4.77. Found: C, 56.83; H, 4.65. For the major product: ¹H NMR (400 MHz): δ 7.77–7.46 (m, 20H, Ph), 5.67 (t, 1H, J = 8.3 Hz, H⁵ or H⁶), 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, CH₂CH₃), 3.85 (dq, 1H, J = 7.1, 3.6 Hz, CH₂CH₃), 3.38 (s, 1H, H¹ or H⁴), 2.63 (d, 1H, J = 7.3 Hz, H¹ or H⁴), 2.33 (s, 3H, Me), 2.15 (d, 3H, J = 1.7 Hz, Me), 1.18 (t, 3H, J = 7.1 Hz, CH₂CH₃), -0.10 to -0.25 (m, 2H, H² and H³). ³¹P NMR (160 MHz): δ 61.3. For the minor product: ¹H 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 H⁵ or H⁶), 4.34 (q, 2H, J = 7.1 Hz, CH_2CH_3), 3.18 (s, 1H, H¹ or H⁴), 2.90 (d, 1H, J = 6.8 Hz, H¹ or H⁴), 2.51 (s, 3H, Me), 1.90 (d, 3H, J = 3.4 Hz, Me₃), 1.37 (t, 3H, J = 7.1 Hz, CH₂CH₃), -0.10 to -0.25 (m, 1H, H² or H³), -0.45 (ddd, 1H, J = 11.7, 9.5, 2.2 Hz, H² or H³). ³¹P NMR (160 MHz): δ 62.5.

X-ray Diffraction Analysis. Crystals of complex **6b-I** suitable for X-ray diffraction were obtained by recrystallization from acetone. The ¹H 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 K α radiation ($\lambda = 0.71069$ Å) at -50 °C in the range 6° < 2 θ < 55° with a scan rate 16° of min⁻¹. Intensities were measured by the $2\theta-\omega$ 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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