Diastereoselective Formation of Ruthenium-Isocyanide and -Acetylide Complexes with Planar-Chiral Cyclopentadienyl-Phosphine Ligands

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The reaction of ruthenium complexes [(η^5:η^1-2-Me-4-R-$C_5H_2CO_2CH_2CH_2PPh_2$)Ru(PR′$_3$)(NCMe)][PF_6] (R = Me, Ph, Bu^t; R′ = Ph, Me, OPh) possessing planar-chiral cyclopentadienyl-phosphine ligands with *tert*-butyl isocyanide resulted in the diastereoselective formation of ruthenium-isocyanide complexes (up to >99% de) under kinetic control. The reaction with phenylacetylene followed by treatment with alumina gave acetylide complexes diastereoselectively (up to >99% de). The configuration of the products was determined by X-ray analyses as well as NOE measurements. In both reactions, the stereochemistry of the ruthenium atom in the substrate did not influence the diastereoselectivity of the products, although the substituent on the cyclopentadienyl ring and the phosphorus ligands on the ruthenium atom showed steric effects on the selectivity.

Introduction

The synthesis and reaction of chiral organometallic complexes have attracted much attention because they provide useful information for the development of new asymmetric catalysts and for furthering our understanding of the mechanism of catalytic asymmetric reactions.[1] Although organometallic complexes with chiral ligands comprise the majority of such chemistry, other types of chiral complexes have become the focus of increasing interest in recent years. A half-sandwich complex with a three-legged piano stool structure generates metal-centered chirality when the ligands differ from each other.[2] Although a significant number of metal-centered chiral complexes have been prepared so far, the control of the stereochemistry at the metal center remains a challenging task.[3]

We have demonstrated that planar-chiral cyclopentadienyl-ruthenium (Cp′Ru) complexes with a tethered phosphine ligand have the ability to control stereochemistry in stoichiometric and catalytic reactions.[4] For example, the reactions of the planar-chiral Cp′Ru complexes with phosphine resulted in the highly selective induction of the metal-centered chirality in the resulting complexes. Because a catalytic reaction involves multistep stoichiometric reactions, further reactions of the metal-centered chiral complexes are of special interest. From this viewpoint, we have recently reported that the reactions of the planar-chiral Cp′Ru complexes with an iodide ligand gave iodo complexes, the metal-centered chirality of which was thermodynamically controlled.[5] We present herein the diastereoselective formation of ruthenium-isocyanide complexes by the ligand exchange reaction of the planar-chiral Cp′Ru complexes under kinetic control. We also examined the reaction with phenylacetylene to give vinylidene complexes, which were isolated as acetylide complexes by treatment with alumina with high diastereoselectivity. Although we used a racemic mixture for each diastereomer of the starting complexes, all structures are given with planar chirality with S_{Cp} for clarity in this article.

Results

Treatment of the diastereomerically pure ruthenium complex [(η^5:η^1-2,4-Me_2-$C_5H_2CO_2CH_2CH_2PPh_2$)Ru(PPh_3)-

(1) *Comprehensive Asymmetric Catalysis I−III*; Jacobsen, E. N., Pflatz, A., Yamamoto, H., Eds.; Springer-Verlag: Berlin, 1999.

(2) For recent reviews, see: (a) Brunner, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1195. (b) Brunner, H. *Eur. J. Inorg. Chem.* **2001**, 905. (c) Ganter, C. *Chem. Soc. Rev.* **2003**, *32*, 130.

(3) For recent references, see: (a) Drommi, D.; Faraone, F.; Francio, G.; Belletti, D.; Graiff, C.; Tiripicchio, A. *Organometallics* **2002**, *21*, 761. (b) Murata, K.; Konishi, H.; Ito, M.; Ikariya, T. *Organometallics* **2002**, *21*, 253. (c) Ritleng, V.; Pfeffer, M.; Sirlin, C. *Organometallics* **2003**, *22*, 347. (d) Faller, J. W.; D'Alliessi, D. G. *Organometallics* **2003**, *22*, 2749. (e) Brunner, H.; Zwack, T.; Zabel, M.; Beck, W.; Böhm, A. *Organometallics* **2003**, *22*, 1741. (f) Pinto, P.; Marconi, G.; Heinemann, F. W.; Zenneck, U. *Organometallics* **2004,** *23*, 374. (g) Davenport, A. J.; Davies, D. L.; Fawcett, J.; Russell, D. R. *Dalton Trans.* **2004**, 1481. (h) Kataoka, Y.; Nakagawa, Y.; Shibahara, A.; Yamagata, T.; Mashima, K.; Tani, K. *Organometallics* **2004**, *23*, 2095. (i) Doppiu, A.; Englert, U.; Salzer, A. *Chem. Commun.* **2004**, 2166. (j) Alezra, V.; Bernardinelli, G.; Corminboeuf, C.; Frey, U.; Kündig, E. P.; Merbach, A. E.; Saudan, C. M.; Viton, F.; Weber, J. *J. Am. Chem. Soc.* **2004**, *126*, 4843. (k) Kataoka, Y.; Shimada, K.; Goi, T.; Yamagata, T.; Mashima, K.; Tani, K. *Inorg. Chim. Acta* **2004**, *357*, 2965. (l) Brunner, H.; Köllnberger, A.; Mehmood, A.; Tsuno, T.; Zabel, M. *Organometallics* **2004**, *23*, 4006. (m) Cayuela, E.; Jalón, F. A.; Manzano, B. R.; Espino, G.; Weissensteiner, W.; Mereiter, K. *J. Am. Chem. Soc.* **2004**, *126*, 7049.

(4) (a) Matsushima, Y.; Onitsuka, K.; Takahashi, S. *Chem. Lett.* **2000**, 760. (b) Onitsuka, K.; Dodo, N.; Matsushima, Y.; Takahashi, S. *Chem. Commun.* **2001**, 521. (c) Onitsuka, K.; Ajioka, Y.; Matsushima, Y.; Takahashi, S. *Organometallics* **2001**, *20*, 3274. (d) Matsushima, Y.; Onitsuka, K.; Kondo, T.; Mitsudo, T.; Takahashi, S. *J. Am. Chem. Soc.* **2001**, *123*, 10405. (e) Matsushima, Y.; Onitsuka, K.; Takahashi, S. *Organometallics* **2004**, *23*, 2439. (f) Matsushima, Y.; Onitsuka, K.; Takahashi, S. *Organometallics* **2004,** *23*, 3763.

(5) Matsushima, Y.; Onitsuka, K.; Takahashi, S. *Dalton Trans.* **2004**, 547.

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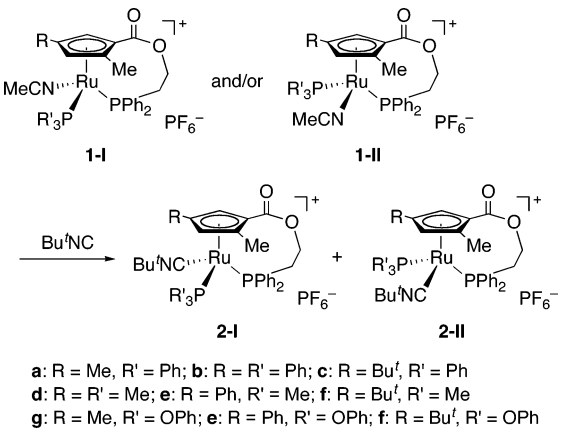
Scheme 1



(NCMe)][PF_6] (**1a-I**), the configuration of which is $S_{Cp}S_{Ru}/R_{Cp}R_{Ru}$,[6] with 10 equiv of *tert*-butyl isocyanide in refluxing dichloromethane for 12 h led to the ligand exchange reaction to give isocyanide complex [(η^5:η^1-2,4-Me_2-$C_5H_2CO_2CH_2CH_2PPh_2$)Ru(PPh_3)($CNBu^t$)][PF_6] (**2a**) in 85% yield (Scheme 1). The ^{31}P NMR spectrum of **2a** clearly showed that the product consisted of two diastereomers, **2a-I** ($S_{Cp}S_{Ru}/R_{Cp}R_{Ru}$) and **2a-II** ($S_{Cp}R_{Ru}/R_{Cp}S_{Ru}$), with 44% de,[6] and the configuration of the major product was determined by differential NOE measurement. The NOE signals of two protons on the Cp′ ring were observed by irradiation of the signal assigned to the methyl group at the 4-position of the Cp′ ring, whereas irradiation of the signal assigned to the methyl group at the 2-position of the Cp′ ring produced NOE signals not only of the Cp′ proton at the 3-position but also of the Bu^t protons on isocyanide. These results clearly suggest that the isocyanide is situated close to the methyl group at the 2-position of the Cp′ ring in the major product. Thus, the major isomer is **2a-II** and the minor one is **2a-I**. When a mixture of the two diastereomers **1a-I** and **1a-II** (75:25) was used as the starting material, complexes **2a-I** and **2a-II** in a 27:73 ratio (46% de) were produced in 83% yield, suggesting that the stereochemistry of the starting material does not influence the diastereoselectivity of the product. This is similar to our previous results in the reaction of complex **1** with Bu_4NI,[5] but is in sharp contrast to the analogous reactions of ruthenium complexes having chiral groups on the Cp′ ring or on the phosphine ligand, which proceed with retention of configuration at the metal center.[7]

Then, we examined the reactions of several ruthenium complexes, the representative results of which are given in Table 1, along with the results described above. The reaction of complex **1b-I**, which has a phenyl group at the 4-position of the Cp′ ring, produced isocyanide complexes **2b-I** and **2b-II** with 80% de (entry 3), and the reaction of a mixture of **1b-I** and **1b-II** in a 90:10 ratio gave essentially the same result (entry 4). By

Table 1. Reactions of 1-I and/or 1-II with *tert*-Butyl Isocyanide[a]

entry	substrate	product	yield/%	de/%[b,c]
1	**1a-I**	**2a**	85	44 (**II**)
2	**1a-I** + **1a-II** (75:25)	**2a**	83	46 (**II**)
3	**1b-I**	**2b**	90	80 (**II**)
4	**1b-I** + **1b-II** (90:10)	**2b**	86	80 (**II**)
5	**1c-I**	**2c**	87	>99 (**I**)
6	**1d-I**	**2d**	93	44 (**II**)
7	**1d-I** + **1d-II** (50:50)	**2d**	90	46 (**II**)
8	**1d-II**	**2d**	88	46 (**II**)
9	**1e-I**	**2e**	88	76 (**II**)
10	**1f-I**	**2f**	89	18 (**I**)
11	**1g-I**	**2g**	85	56 (**II**)
12	**1h-I**	**2h**	85	34 (**II**)
13	**1i-I**	**2i**	81	76 (**I**)

[a] Reaction conditions: CH_2Cl_2, reflux, 12 h (entries 1−5); CH_2Cl_2, reflux, 36 h (entries 6−10); $ClCH_2CH_2Cl$, reflux, 12 h (entries 11−13). [b] Determined by ^{31}P NMR. [c] The symbol in parentheses indicates the configuration of the major products as determined by NOE measurement and X-ray crystallography.

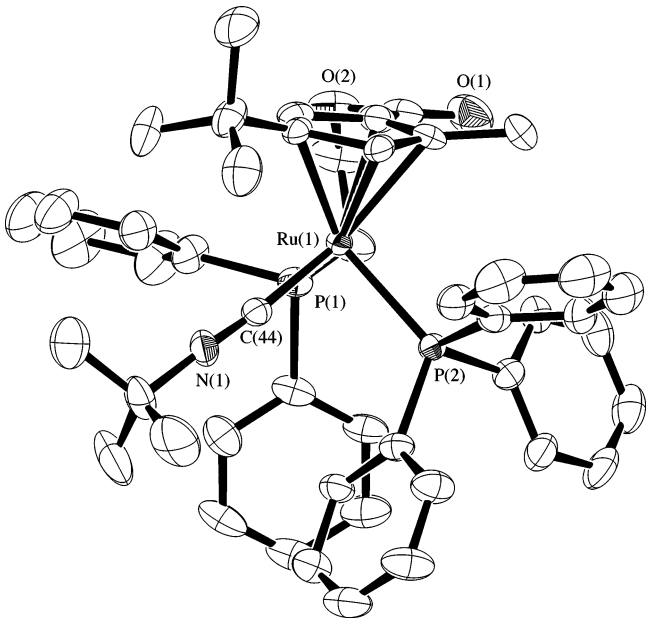


Figure 1. ORTEP drawing of complex **2c-I**. Hydrogen atoms and counteranion PF_6^- are omitted for clarity.

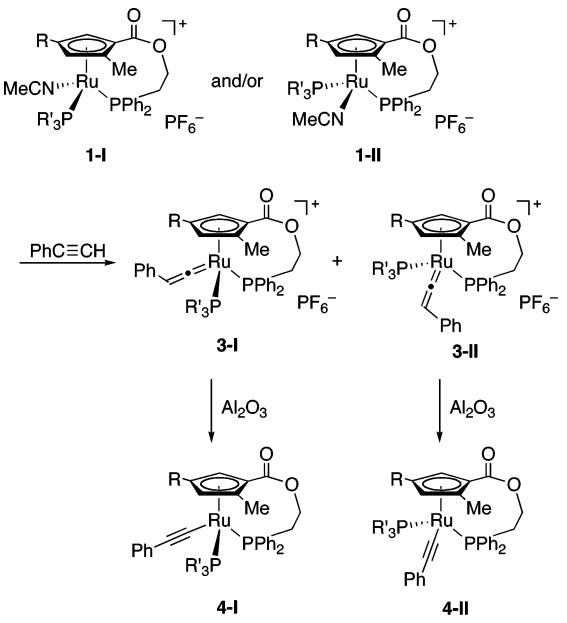
contrast, the reaction of Bu^t analogue **1c-I** produced a single diastereomer (**2c-I**), the configuration at the metal of which is opposite of those of the major isomers from complexes **2a** and **2b** (entry 5). The structure of complex **2c-I** was unequivocally determined by X-ray crystallography (Figure 1).

As the reactivities of trimethylphosphine (**1d**−**f**) and triphenylphosphite (**1g**−**i**) complexes toward *tert*-butyl isocyanide were lower than those of triphenyphosphine analogues **1a**−**c**, slightly severe conditions were required for improving the yield of isocyanide complexes. Thus, complexes **1d**−**f** were reacted with *tert*-butyl isocyanide for 36 h, and the reactions of complexes **1g**−**i** were performed in refluxing 1,2-dichloroethane. The reactions of **1d-I** and/or **1d-II** gave a mixture of isocyanide complexes **2d-I** and **2d-II** in good yields, and the selectivity of **2d-I** and **2d-II** was also independent of the stereochemistry of the substrate (entries 6−8). Complex **2e-II** was obtained as a major isomer from the reaction of **1e-I** (entry 9). Although the structure of the major isomer produced in the reaction of **1f-I** was

(6) The assignment for the absolute configuration at the metal center (*R* or *S*) in complexes with trimethylphosphine is opposite those of triphenylphosphine and triphenylphosphite with the same structure due to the difference in the sequence of the tethered phosphine and the phosphorus ligand.

(7) (a) Morandini, F.; Consiglio, G.; Lucchini, V. *Organometallics* **1985**, *4*, 1202. (b) Cesarotti, E.; Walker, M. A. P. C.; Hursthouse, M. B.; Vefghi, R.; Schofield, P. A.; White, C. *J. Organomet. Chem.* **1985**, *286*, 343.

Scheme 2



a: R = Me, R' = Ph; **b**: R = R' = Ph; **c**: R = Bu^t, R' = Ph
d: R = R' = Me; **e**: R = Ph, R' = Me; **f**: R = Bu^t, R' = Me

different from those of **1d-I** and **1e-I**, as observed in the triphenyphosphine analogue, the diastereoselectivity of **2f-I** was much lower than that of **2c-I** (entry 10). A similar tendency was observed for the diastereoselectivity in the reactions of **1g**−**i** (entries 11−13).

Recrystallization of a mixture of **2a-I** and **2a-II** in a 28:72 ratio from dichloromethane−diethyl ether led to a change of the diastereomeric ratio to 83:17. It is noteworthy that the diastereomeric ratio was not changed by refluxing the mixture of **2a-I** and **2a-II** (83:17) in dichloromethane for 12 h. Although similar treatments were performed in the presence of isocyanide and acetonitrile, no epimerization was detected. These results contrast the fact that epimerization between two diastereomers was observed in analogous iodo complexes.[5]

Next, we examined the diastereoselectivity in the formation of the ruthenium-vinylidene complex, which is known to be an important intermediate in some catalytic reactions.[8] Treatment of **1a-I** with 10 equiv of phenylacetylene in dichloromethane under reflux gave vinylidene complex **3a** in a diastereometically pure form (Scheme 2).[9] However, the isolation of vinylidene complex **3a** was unsuccessful. Thus, vinylidene complex **3a** was converted into acetylide complex **4a** by treatment with alumina.[10] Complex **4a** was formed as a single diastereomer, the structure of which was determined by X-ray analysis. As shown in Figure 2, complex **4a** has the configuration $S_{Cp}S_{Ru}/R_{Cp}R_{Ru}$ (**4a-I**). The reaction of a mixture of the two diastereomers **1a-I** and **1a-II** (75:25) gave complex **3a** as a single diastereomer, which was also isolated after conversion into acetylide complex **4a-I** in 85% yield, suggesting that the stereochemistry of the starting material does not influence the diastereoselectivity of the product. This result is similar to that observed in isocyanide complexes **2** (see above), but is in sharp contrast to the known chemistry of analogous ruthenium complexes with a chiral phosphine ligand, which stereospecifically produce the vinylidene complexes with retention of configuration at the ruthenium atom.[9]

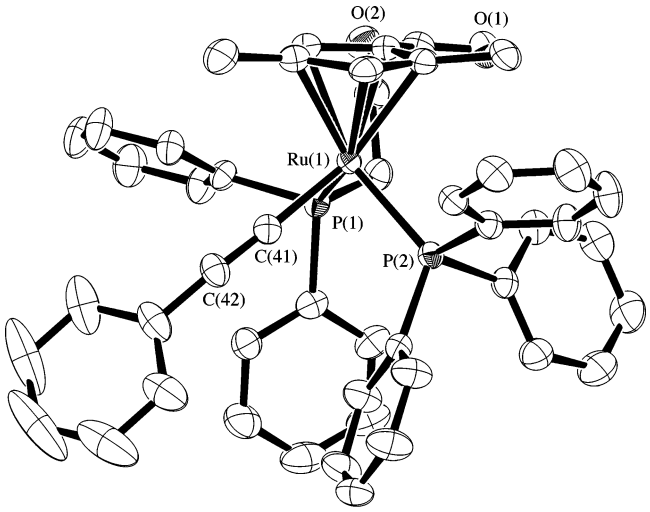


Figure 2. ORTEP drawing of complex **4a-I**. Hydrogen atoms and solvate are omitted for clarity.

Table 2. Reactions of 1-I and/or 1-II with Phenylacetylene[a]

entry	substrate	product	yield/%	de/%[b,c]
1	**1a-I**	**4a**	89	>99 (**I**)
2	**1a-I** + **1a-II** (75:25)	**4a**	85	>99 (**I**)
3	**1b-I**	**4b**	90	>99[d]
4	**1b-I** + **1b-II** (90:10)	**4b**	92	>99[d]
5[e]	**1c-I**	**4c**	91	>99 (**I**)
6	**1d-I**	**4d**	87	74 (**II**)
7	**1d-I** + **1d-II** (50:50)	**4d**	94	70 (**II**)
8	**1d-II**	**4d**	96	74 (**II**)
9	**1e-I**	**4e**	82	70 (**II**)
10	**1f-I**	**4f**	92	40 (**I**)

[a] Reaction conditions: CH_2Cl_2, reflux, 48 h. [b] Determined by ^{31}P NMR. [c] The symbol in parentheses indicates the configuration of the major products as determined by NOE measurement and X-ray crystallography. [d] The configuration of the major products could not be determined. [e] Reaction conditions: CH_2Cl_2, room temperature, 48 h.

Table 2 gives the representative results of the reactions of **1-I** and/or **1-II** with phenylacetylene followed by treatment with alumina to give acetylide complexes **4-I** and/or **4-II**. We also examined the diastereoselectivity of vinylidene complex **3** by measuring ^{31}P NMR spectra of the reaction mixture before treatment with alumina and found the diastereoselectivity of **4** was essentially the same as that of **3**. It seems to be reasonable that the transformation of **3** into **4** proceeds with retention of configuration at the ruthenium atom, because no bond cleavage around the ruthenium atom is required in this step. Although the reaction of complex **1b** produced a single diastereomer (**4b**), the stereochemistry of **4b** could not be determined (entries 3 and 4). Upon treatment of complex **1c-I**, a single diastereomer

(8) For recent reviews, see: (a) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311. (b) Katayama, H.; Ozawa, F. *Coord. Chem. Rev.* **2004**, *248*, 1703.

(9) (a) Consiglio, G.; Morandini, F.; Ciani, G. F.; Sironi, A. *Organometallics* **1986**, *5*, 1976. (b) Consiglio, G.; Morandini, F. *Inorg. Chim. Acta* **1987**, *127*, 79. (c) Slugovc, C.; Simanko, W.; Mereiter, K.; Schmid, R.; Kirchner, K.; Xiao, L.; Weissensteiner, W. *Organometallics* **1999**, *18*, 3865.

(10) Hodge, A. J.; Ingham, S. L.; Kakkar, A. K.; Khan, M. S.; Lewis, J.; Long, N. J.; Parker, D. G.; Raithby, P. R. *J. Organomet. Chem.* **1995**, *488*, 205.

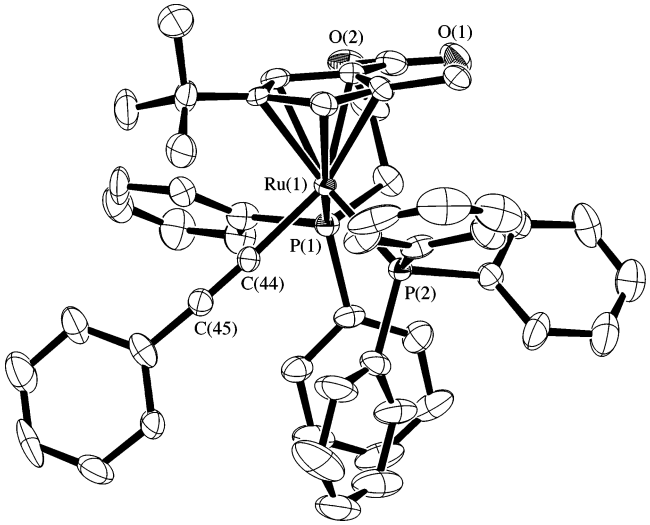


Figure 3. ORTEP drawing of complex **4c-I**. Hydrogen atoms are omitted for clarity.

(**4c-I**) was also obtained (entry 5), and the stereochemistry was confirmed by X-ray analysis, as shown in Figure 3. Although complexes **1d**−**f** were also reacted with phenylacetylene to give analogous acetylide complexes (**4d**−**f**) as mixtures of two diastereomers, the configuration at the ruthenium atom of the major product was opposite that of triphenylphosphine analogues (entries 6−10). Similar reactions of complexes **1g**−**i** did not produce any acetylide complexes at all, and the starting materials were recovered quantitatively. When the reaction was performed in refluxing 1,2-dichloroethane, the product was a complex mixture from which no acetylide complex could be isolated.

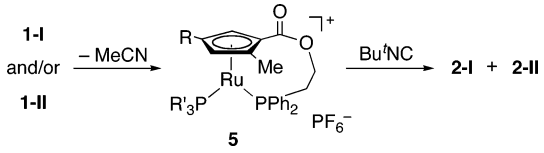
A diastereomerically pure sample of **4d-II** was obtained by recrystallization of a mixture of **4d-I** and **4d-II** (13:87) from dichloromethane−hexane. When complex **4d-II** was refluxed in dichloromethane for a long time, no epimerization took place, as observed for **2a-I** and **2a-II**.[11]

Discussion

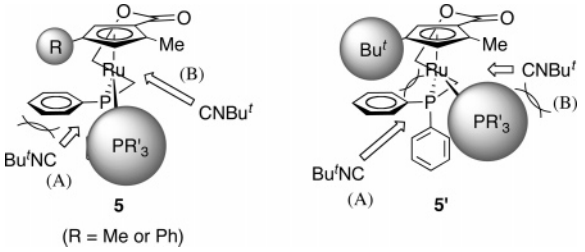
Because no epimerization between the two diastereomers **2a-I** and **2a-II** was detected, isocyanide complex **2** was not in equilibrium depending on the thermodynamic stability of the diastereomers. Thus, the diastereoselectivity of isocyanide complex **2** is not under thermodynamic control but under kinetic control. Although it may seem unique that the diastereoselectivity was not affected by the stereochemistry of the starting material, there are two possible interpretations for this. One is that the epimerization between **1-I** and **1-II** is much faster than the ligand exchange reaction with isocyanide, and the other is the formation of an intermediate that has no metal-centered chirality. Although slow epimerization between **1-I** and **1-II** was observed for **1a** and **1b**, no epimerization was detected for **1d**.[4b] The results of the reactions using **1d-I** and/or **1d-II** clearly suggest that the latter interpretation is plausible. Thus, a coordinatively unsaturated complex (**5**) is generated by the dissociation of acetonitrile, and *tert*-butyl isocyanide coordinates to **5**, giving **2** (Scheme 3).[9c]

(11) Carmona, D.; Vega, C.; Lahoz, F. J.; Atencio, R.; Oro, L. A.; Lamata, M. P.; Viguri, F.; José, E. S. *Organometallics* **2000**, *19*, 2273.

Scheme 3



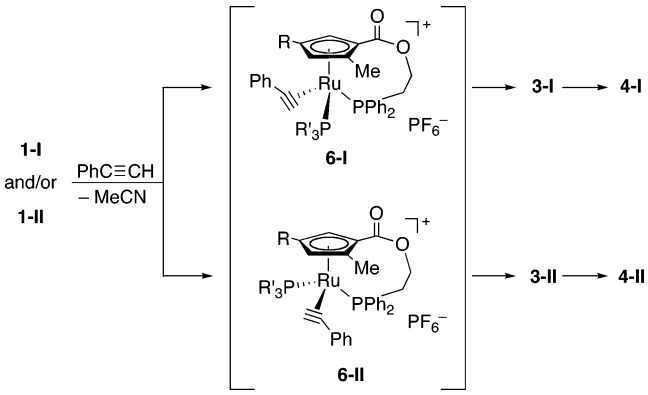
Scheme 4



The results in Table 1 suggest that the diastereoselectivity of **2** depended on the substituent at the 4-position of the Cp′ ring and the phosphorus ligand. The bulky substituent, Bu^t, on the Cp′ ring and the bulky phosphorus ligands, such as PPh_3 and $P(OPh)_3$, led to the increase in the selectivity of **2-I**, whereas the combination of the small substituent, Me and Ph, and phosphorus ligand, PMe_3, selectively produced **2-II**. These steric effects may be reasonably explained by using intermediate **5**, which has a two-legged piano stool structure (Scheme 4). The approach of isocyanide to the ruthenium atom of **5** from side A gives **2-I**, whereas the coordination from side B produces **2-II**. As one of the two phenyl rings on the tethered phosphine ligand protrudes equatorially, the approach of isocyanide from side A is affected by steric hindrance. Consequently, the approach from side B is faster than that from A, resulting in the selective formation of **2-II**. This explanation is applicable to the results obtained from the combination of a small substituent and a small phosphorus ligand. Although the Bu^t group on the Cp′ ring would provide an adverse effect on the attack from side A, the selectivity of **2-I** was higher than those in the reactions of **1**, having a Me or a Ph group on the Cp′ ring. In particular, **2c-I** was obtained as a sole product in the reaction of **1c-I**, which had a bulky phosphine ligand. This inverse selectivity is likely caused by the structural change of the intermediate (**5′**) due to the steric repulsion between the Bu^t group on the Cp′ ring and the phosphorus ligand. Thus, the phosphorus ligand is located apart from the Bu^t group and effectively blocks the attack from side B. This explanation is consistent with the fact that the selectivity of **2-I** increases with increasing bulkiness of the phosphorus ligand.

The diastereoselectivity of acetylide complex **4** must be determined in the step for forming vinylidene complex **3**, because the transformation of **3** into **4** proceeded with maintenance of the diastereomeric ratio and no epimerization took place in **4**. Although we conducted several experiments to determine whether the diastereoselectivity of **3** was under kinetic or thermodynamic control, no conclusive results were obtained. The results in Table 2 show the steric effect of the substituent on the Cp′ ring and the phosphorus ligand on the diastereoselectivity of **4**, similar to that for **2**. However, if the selectivity were to depend on the thermodynamic stability of the resulting vinylidene complexes **3**, a more

Scheme 5



sterically demanding substituent and phosphorus ligand would produce **3-I** because the steric repulsion between the substituent on the Cp′ ring and the phosphorus ligand is important.[5] The results in Table 2 are also in agreement with this explanation. Therefore, the factor contributing to the stereochemistry of **4** is still unclear.

Although the stereochemistry of **4b** could not be determined, the diastereoselectivity of triphenylphosphine complexes **4a**−**c** was very high compared to that of trimethylphosphine derivatives **4d**−**e**. This phenomenon is likely due to the steric factor of the phosphine ligand, because the selectivity of **4-I** in **4f** is much higher than those in **4d** and **4e**. It is well known that the η^2-alkyne complex is generated as an intermediate in the formation of the vinylidene complex. As the coordination sphere of η^2-alkyne intermediate **6** is fairly crowded, the steric effect of the phosphine ligand would be enhanced (Scheme 5).

Summary

We have described the diastereoselective formation of ruthenium-isocyanide and -vinylidene complexes, the latter of which were isolated as acetylide complexes. The planar-chiral cyclopentadienyl-phosphine ligand showed high ability to control the stereochemistry at the metal center in the resulting ruthenium complexes, whereas the metal-centered chirality of the starting complexes had no influence on the diastereoselectivity. A significant steric effect of the substituent on the Cp′ ring and the phosphorus ligand was observed in both reactions. Because the complexes prepared here have potential applications in other reactions, the results should be useful for developing the stereoselective transformation of isocyanides and acetylenes. Further studies that focus on the application to asymmetric catalysis are in progress.

Experimental Section

All reactions were carried out under an argon atmosphere, but the workup was performed in air. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured on JEOL JNM-EX270, -LA400, and -LA600 spectrometers using acetone-d_6 for isocyanide complexes and $CDCl_3$ for acetylide complexes as a solvent. Chemical shifts are given in ppm based on $SiMe_4$ as an internal standard for ^{1}H and ^{13}C NMR, and 85% H_3PO_4 as an external standard for ^{31}P NMR. IR and mass spectra were taken on a Perkin-Elmer system 2000 FT-IR and JEOL JMS-600H instrument, respectively. Elemental analyses were performed by the Material Analysis Center, ISIR, Osaka University.

Ruthenium complexes **1a**−**i** were prepared by the method previously reported.[4b,12] All other chemicals available commercially were used without further purification.

Reaction of [(η^5:η^1-2-Me-4-R-$C_5H_2CO_2CH_2CH_2PPh_2$)Ru(PPh$_3$)(NCMe)][PF$_6$] (R = Me, Ph, Bu^t) 1a−c with *tert*-Butyl Isocyanide. To a solution of ruthenium complex **1** (0.10 mmol) in dichloromethane (5 mL) was added *tert*-butyl isocyanide (80 mg, 1.0 mmol), and the reaction mixture was refluxed for 12 h. After removal of the solvent under reduced pressure, the residual oil was washed with diethyl ether several times. The crude product was purified by silica gel column chromatography using a mixture of dichloromethane−acetone (v/v = 5/1) as eluent to give red solid. Yield and diastereoselectivity of the product **2** are given in Table 1.

[(η^5:η^1-2,4-Me$_2$-$C_5H_2CO_2CH_2CH_2PPh_2$)Ru(PPh$_3$)(CNBu^t)][PF$_6$] (2a-I and 2a-II). IR (cm^{-1}, KBr): 2143 ($\nu_{C\equiv N}$), 1722 ($\nu_{C=O}$). FAB-MS: *m/z* 796 (M − PF_6^-). Anal. Calcd for $C_{45}H_{46}F_6NO_2P_3Ru$: C, 57.45; H, 4.93; N, 1.49. Found: C, 57.37; H, 4.98; N, 1.69. **Major product (2a-I):** ^{1}H NMR (400 MHz): δ 7.88−7.33 (m, 17H, Ph), 6.95−6.90 (m, 6H, Ph), 6.63−6.58 (m, 2H, Ph), 5.85 (s, 1H, Cp′), 4.94 (ddd, 1H, J = 23.7, 11.2, 7.1 Hz, OCH_2), 4.49 (s, 1H, Cp′), 3.70−3.64 (m, 1H, OCH_2), 3.11−3.02 (m, 1H, PCH_2), 2.93−2.81 (m, 1H, PCH_2), 2.52 (s, 3H, Cp′*Me*), 1.68 (s, 3H, Cp′*Me*), 1.45 (s, 9H, CMe_3). ^{13}C NMR (151 MHz): δ 165.6 (C═O), 141.6−129.1 (Ph), 117.8 (Cp′), 104.1 (Cp′), 94.3 (Cp′), 89.3 (Cp′), 83.6 (d, J = 7 Hz, Cp′), 66.0 (*C*Me_3), 59.7 (OCH_2), 30.6 (C*Me*$_3$), 25.3 (d, J = 34 Hz, PCH_2), 13.3 (Cp′*Me*), 12.2 (Cp′*Me*); the signal assignable to the isocyano-carbon could not be detected. ^{31}P NMR (162 MHz): δ 47.7 (d, J = 27 Hz), 36.4 (d, J = 27 Hz). **Minor product (2a-II):** ^{1}H NMR (400 MHz): δ 7.88−7.33 (m, 23H, Ph), 6.24−6.19 (m, 2H, Ph), 5.17−5.07 (m, 1H, OCH_2), 4.84 (s, 1H, Cp′), 4.78 (s, 1H, Cp′), 4.09−4.02 (m, 1H, OCH_2), 2.93−2.81 (m, 1H, PCH_2), 2.72−2.63 (m, 1H, PCH_2), 2.41 (s, 3H, Cp′*Me*), 1.35 (d, 3H, J = 2.9 Hz, Cp′*Me*), 1.23 (s, 9H, CMe_3). ^{31}P NMR (162 MHz): δ 46.1 (d, J = 26 Hz), 38.0 (d, J = 26 Hz).

[(η^5:η^1-2-Me-4-Ph-$C_5H_2CO_2CH_2CH_2PPh_2$)Ru(PPh$_3$)(CNBu^t)][PF$_6$] (2b-I and 2b-II). IR (cm^{-1}, KBr): 2137 ($\nu_{C\equiv N}$), 1715 ($\nu_{C=O}$). FAB-MS: *m/z* 858 (M − PF_6^-). Anal. Calcd for $C_{50}H_{48}F_6NO_2P_3Ru$: C, 59.88; H, 4.82; N, 1.40. Found: C, 60.05; H, 4.92; N, 1.40. **Major product (2b-I):** ^{1}H NMR (270 MHz): δ 7.76−7.22 (m, 20H, Ph), 7.01 (d, 2H, J = 7.1 Hz, Ph), 6.60−6.40 (m, 8H, Ph), 6.15 (s, 1H, Cp′), 5.18−5.02 (m, 1H, OCH_2), 5.10 (s, 1H, Cp′), 4.08−3.98 (m, 1H, OCH_2), 3.17−3.08 (m, 2H, PCH_2), 2.65 (s, 3H, Cp′*Me*), 1.43 (s, 9H, CMe_3). ^{13}C NMR (151 MHz): δ 165.5 (C═O), 141.5−127.3 (Ph), 113.2 (Cp′), 104.7 (Cp′), 92.6 (d, J = 10 Hz, Cp′), 91.5 (Cp′), 78.0 (d, J = 7 Hz, Cp′), 66.0 (*C*Me_3), 59.7 (OCH_2), 30.6 (C*Me*$_3$), 23.2 (d, J = 35 Hz, PCH_2), 13.5 (Cp′*Me*); the signal assignable to the isocyano-carbon could not be detected. ^{31}P NMR (162 MHz): δ 42.9 (d, J = 26 Hz), 35.1 (d, J = 26 Hz). **Minor product (2b-II):** ^{1}H NMR (270 MHz): δ 7.99 (d, 2H, J = 7.4 Hz, Ph), 7.90 (br, 2H, Ph), 7.70−7.11 (m, 26H, Ph), 5.44 (s, 1H, Cp′), 5.37 (s, 1H, Cp′), 5.21−5.14 (m, 1H, OCH_2), 4.11−4.07 (m, 1H, OCH_2), 2.95−2.88 (m, 1H, PCH_2), 2.77−2.73 (m, 1H, PCH_2), 0.72 (s, 9H, CMe_3). ^{31}P NMR (162 MHz): δ 46.9 (d, J = 25 Hz), 38.8 (d, J = 25 Hz).

[(η^5:η^1-2-Me-4-Bu^t-$C_5H_2CO_2CH_2CH_2PPh_2$)Ru(PPh$_3$)(CNBu^t)][PF$_6$] (2c-II). ^{1}H NMR (400 MHz): δ 8.02−7.98 (m, 2H, Ph), 7.67−7.11 (m, 21H, Ph), 6.23 (t, 2H, J = 8.5 Hz, Ph), 5.19−5.09 (m, 1H, OCH_2), 5.01−4.99 (m, 1H, Cp′), 4.51−4.49 (m, 1H, Cp′), 3.90−3.83 (m, 1H, OCH_2), 3.18−3.09 (m, 1H, PCH_2), 2.68 (dt, 1H, J = 15.4, 4.6 Hz, PCH_2), 1.59 (s, 9H, CMe_3), 1.59 (d, 3H, J = 2.7 Hz, Cp′*Me*), 1.14 (s, 9H, CMe_3). ^{13}C NMR (151 MHz): δ 166.8 (C═O), 147.8−129.0 (Ph), 114.1 (Cp′), 91.5 (Cp′), 87.5 (d, J = 10 Hz, Cp′), 74.6 (d, J = 7 Hz, Cp′), 66.0 (Cp′), 60.4 (*C*Me_3), 60.3 (OCH_2), 33.3 (C*Me*$_3$),

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31.2 (C*Me*$_3$), 20.4 (d, J = 30 Hz, PCH$_2$), 12.2 (Cp′*Me*); the signal assignable to the isocyano carbon could not be detected. ^{31}P NMR (162 MHz): δ 48.0 (d, J = 25 Hz), 33.2 (d, J = 25 Hz). IR (cm^{-1}, KBr): 2127 ($\nu_{C\equiv N}$), 1713 ($\nu_{C=O}$). FAB-MS: *m/z* 838 (M − PF_6^-). Anal. Calcd for $C_{48}H_{52}F_6NO_2P_3Ru$: C, 58.65; H, 5.33; N, 1.42. Found: C, 58.75; H, 5.36; N, 1.66.

Reaction of [(η^5:η^1-2-Me-4-R-$C_5H_2CO_2CH_2CH_2PPh_2$)Ru(PMe$_3$)(NCMe)][PF_6] (R = Me, Ph, Bu^t) (1d−f) with *tert*-Butyl Isocyanide. This reaction was performed in a manner similar to that for **1a**−**c** with a longer reaction time (36 h). Yield and diastereoselectivity of the products are given in Table 1.

[(η^5:η^1-2,4-Me$_2$-$C_5H_2CO_2CH_2CH_2PPh_2$)Ru(PMe$_3$)(CNBu^t)][PF_6] (2d-I and 2d-II). IR (cm^{-1}, KBr): 2126 ($\nu_{C\equiv N}$), 1705 ($\nu_{C=O}$). FAB-MS: *m/z* 610 (M − PF_6^-). Anal. Calcd for $C_{30}H_{40}F_6NO_2P_3Ru$: C, 47.75; H, 5.34; N, 1.86. Found: C, 47.90; H, 5.24; N, 1.88. **Major product (2d-I):** ^{1}H NMR (600 MHz): δ 7.78−7.63 (m, 4H, Ph), 7.46 (br, 4H, Ph), 7.13 (br, 2H, Ph), 5.22 (s, 1H, Cp′), 5.11 (s, 1H, Cp′), 5.06−5.00 (m, 1H, OCH$_2$), 3.96−3.92 (m, 1H, OCH$_2$), 2.94−2.80 (m, 2H, PCH$_2$), 2.42 (s, 3H, Cp′*Me*), 2.31 (d, 3H, J = 2.6 Hz, Cp′*Me*), 1.65 (s, 9H, CMe$_3$), 1.14 (d, 9H, J = 9.9 Hz, PMe$_3$). ^{13}C NMR (151 MHz): δ 164.9 (C═O), 140.7−129.8 (Ph), 115.5 (Cp′), 104.0 (Cp′), 93.3 (Cp′), 85.6 (d, J = 9 Hz, Cp′), 82.3 (d, J = 6 Hz, Cp′), 59.4 (*C*Me$_3$), 59.3 (OCH$_2$), 30.8 (C*Me*$_3$), 23.0 (d, J = 35 Hz, PCH$_2$), 20.0 (d, J = 34 Hz, PMe$_3$), 13.7 (Cp′*Me*), 13.4 (Cp′*Me*); the signal assignable to the isocyano carbon could not be detected. ^{31}P NMR (162 MHz): δ 45.3 (d, J = 32 Hz), 10.2 (d, J = 32 Hz). **Minor product (2d-II):** ^{1}H NMR (600 MHz): δ 7.88−7.85 (m, 2H, Ph), 7.78−7.63 (m, 6H, Ph), 7.37 (br, 2H, Ph), 5.18 (s, 1H, Cp′), 5.06−5.00 (m, 1H, OCH$_2$), 4.95 (s, 1H, Cp′), 3.96−3.92 (m, 1H, OCH$_2$), 3.21−3.15 (m, 1H, PCH$_2$), 2.94−2.80 (m, 1H, PCH$_2$), 2.39 (d, 3H, J = 3.9 Hz, Cp′*Me*), 2.34 (s, 3H, Cp′*Me*), 1.54 (s, 9H, CMe$_3$), 1.12 (d, 9H, J = 9.9 Hz, PMe$_3$). ^{31}P NMR (162 MHz): δ 43.1 (d, J = 31 Hz), 10.8 (d, J = 31 Hz).

[(η^5:η^1-2-Me-4-Ph-$C_5H_2CO_2CH_2CH_2PPh_2$)Ru(PMe$_3$)(CNBu^t)][PF_6] (2e-I and 2e-II). IR (cm^{-1}, KBr): 2128 ($\nu_{C\equiv N}$), 1715 ($\nu_{C=O}$). FAB MS: *m/z* 672 (M − PF_6^-). Anal. Calcd for $C_{35}H_{42}F_6NO_2P_3Ru$: C, 51.47; H, 5.18; N, 1.72. Found: C, 51.47; H, 5.06; N, 1.64. **Major product (2e-I):** ^{1}H NMR (400 MHz): δ 7.92 (d, 2H, J = 7.3 Hz, Ph), 7.77−7.73 (m, 5H, Ph), 7.64 (t, 2H, J = 7.3 Hz, Ph), 7.55 (t, 1H, J = 7.3 Hz, Ph), 7.44−7.43 (m, 3H, Ph), 7.11−7.07 (m, 2H, Ph), 6.00 (s, 1H, Cp′), 5.79 (s, 1H, Cp′), 5.15−5.05 (m, 1H, OCH$_2$), 4.12−4.08 (m, 1H, OCH$_2$), 3.00−2.95 (m, 2H, PCH$_2$), 2.55 (s, 3H, Cp′*Me*), 1.67 (s, 9H, CMe$_3$), 0.82 (d, 9H, J = 10.3 Hz, PMe$_3$). ^{13}C NMR (151 MHz): δ 165.0 (C═O), 140.4−127.2 (Ph), 115.9 (Cp′), 106.2 (Cp′), 89.4 (Cp′), 84.0 (d, J = 6 Hz, Cp′), 80.8 (Cp′), 59.7 (*C*Me$_3$), 59.6 (d, J = 5 Hz, OCH$_2$), 30.2 (C*Me*$_3$), 22.8 (d, J = 35 Hz, PCH$_2$), 18.8 (d, J = 34 Hz, PMe$_3$), 14.0 (Cp′*Me*); the signal assignable to the isocyano carbon could not be detected. ^{31}P NMR (162 MHz): δ 44.6 (d, J = 32 Hz), 10.5 (d, J = 32 Hz). **Minor product (2e-II):** ^{31}P NMR (162 MHz): δ 44.0 (d, J = 30 Hz), 12.1 (d, J = 30 Hz).

[(η^5:η^1-2-Me-4-Bu^t-$C_5H_2CO_2CH_2CH_2PPh_2$)Ru(PPh$_3$)(CNBu^t)][PF_6] (2f-I and 2f-II). IR (cm^{-1}, KBr): 2112 ($\nu_{C\equiv N}$), 1715 ($\nu_{C=O}$). FAB-MS: *m/z* 652 (M − PF_6^-). Anal. Calcd for $C_{33}H_{46}F_6NO_2P_3Ru$: C, 49.75; H, 5.82; N, 1.76. Found: C, 49.55; H, 5.74; N, 1.74. **Major product (2f-II):** ^{1}H NMR (400 MHz): δ 8.00−7.95 (m, 2H, Ph), 7.63−7.47 (m, 6H, Ph), 7.37 (br, 2H, Ph), 5.19 (s, 1H, Cp′), 5.17 (s, 1H, Cp′), 5.07−4.97 (m, 1H, OCH$_2$), 3.76−3.69 (m, 1H, OCH$_2$), 3.08−2.81 (m, 2H, PCH$_2$), 2.40 (s, 3H, Cp′*Me*), 1.51 (s, 9H, CMe$_3$), 1.50 (s, 9H, CMe$_3$), 1.14 (d, 9H, J = 10.3 Hz, PMe$_3$). ^{13}C NMR (151 MHz): δ 166.5 (C═O), 140.9−129.2 (Ph), 111.7 (Cp′), 92.4 (Cp′), 89.9 (Cp′), 80.3 (d, J = 7 Hz, Cp′), 77.1 (d, J = 6 Hz, Cp′), 60.3 (*C*Me$_3$), 59.9 (OCH$_2$), 33.8 (*C*Me$_3$), 32.1 (C*Me*$_3$), 31.3 (C*Me*$_3$), 22.4 (d, J = 34 Hz, PCH$_2$), 18.8 (d, J = 32 Hz, PMe$_3$), 13.2 (Cp′*Me*); the signal assignable to the isocyano carbon could not be detected. ^{31}P NMR (162 MHz): δ 41.7 (d, J = 31 Hz), 8.3 (d, J = 31 Hz). **Minor product (2f-I):** ^{1}H NMR (400 MHz): δ 7.91−7.86 (m, 2H, Ph), 7.70−7.68 (m, 1H, Ph), 7.63−7.47 (m, 5H, Ph), 7.19 (br, 2H, Ph), 5.38 (s, 1H, Cp′), 5.27 (s, 1H, Cp′), 5.07−4.97 (m, 1H, OCH$_2$), 4.05 (br, 1H, OCH$_2$), 3.08−2.81 (m, 2H, PCH$_2$), 2.41 (s, 3H, Cp′*Me*), 1.66 (s, 9H, CMe$_3$), 1.45 (s, 9H, CMe$_3$), 1.21 (d, 9H, J = 9.8 Hz, PMe$_3$). ^{31}P NMR (162 MHz): δ 40.3 (d, J = 30 Hz), 10.4 (d, J = 30 Hz).

Reaction of [(η^5:η^1-2-Me-4-R−$C_5H_2CO_2CH_2CH_2PPh_2$)-Ru{P(OPh)$_3$}(NCMe)][PF_6] (R = Me, Ph, Bu^t) (1g−i) with *tert*-Butyl Isocyanide. Ruthenium complexes **1g**−**i** (0.1 mmol) were treated with *tert*-butyl isocyanide (0.08 g, 1.0 mmol) in refluxing 1,2-dichloroethane (5 mL) for 12 h. Purification similar to that for **1a**−**c** gave the products in yields with diastereoselectivity given in Table 1, respectively.

[(η^5:η^1-2,4-Me$_2$-$C_5H_2CO_2CH_2CH_2PPh_2$)Ru{P(OPh)$_3$}(CNBu^t)][PF_6] (2g-I and 2g-II). IR (cm^{-1}, KBr): 2161 ($\nu_{C\equiv N}$), 1722 ($\nu_{C=O}$). FAB-MS: *m/z* 844 (M − PF_6^-). Anal. Calcd for $C_{45}H_{46}F_6NO_5P_3Ru$: C, 54.66; H, 4.69; N, 1.42. Found: C, 54.44; H, 4.66; N, 1.67. **Major product (2g-I):** ^{1}H NMR (600 MHz): δ 7.98−7.95 (m, 2H, Ph), 7.68−7.67 (m, 3H, Ph), 7.55−7.52 (m, 2H, Ph), 7.48−7.46 (m, 1H, Ph), 7.41−7.38 (m, 2H, Ph), 7.24−7.21 (m, 6H, Ph), 7.12 (t, 3H, J = 7.5 Hz, Ph), 6.76 (d, 6H, J = 8.6 Hz, Ph), 5.19 (s, 1H, Cp′), 5.14−5.08 (m, 1H, OCH$_2$), 4.14−4.09 (m, 1H, OCH$_2$), 4.07 (s, 1H, Cp′), 3.09−3.02 (m, 2H, PCH$_2$), 2.43 (d, 3H, J = 3.8 Hz, Cp′*Me*), 2.23 (s, 3H, Cp′*Me*), 1.71 (s, 9H, CMe$_3$). ^{13}C NMR (151 MHz): δ 164.6 (C═O), 152.6 (C≡N), 140.1−121.2 (Ph), 116.5 (Cp′), 106.0 (Cp′), 94.2 (Cp′), 86.0 (d, J = 7 Hz, Cp′), 83.6 (d, J = 14 Hz, Cp′), 60.2 (*C*Me$_3$), 59.8 (d, J = 5 Hz, OCH$_2$), 30.9 (C*Me*$_3$), 23.2 (d, J = 35 Hz, PCH$_2$), 13.4 (Cp′*Me*), 13.3 (Cp′*Me*). ^{31}P NMR (162 MHz): δ 133.2 (d, J = 52 Hz), 42.9 (d, J = 52 Hz). **Minor product (2g-II):** ^{1}H NMR (600 MHz): δ 2.41 (s, 3H, Cp′*Me*), 2.26 (d, 3H, J = 3.4 Hz, Cp′*Me*), 1.64 (s, 9H, CMe$_3$); the signals assignable to the other protons could not be identified due to overlap with those of the major product. ^{31}P NMR (162 MHz): δ 132.2 (d, J = 55 Hz); the other signal could not be detected due to overlap with that of the major product.

[(η^5:η^1-2-Me-4-Ph-$C_5H_2CO_2CH_2CH_2PPh_2$)Ru{P(OPh)$_3$}(CNBu^t)][PF_6] (2h-I and 2h-II). ^{13}C NMR (151 MHz): δ 164.9 (C═O), 164.6 (C═O), 152.4 (d, J = 15 Hz, C≡N), 152.3 (d, J = 14 Hz, C≡N), 139.9−120.8 (Ph), 116.7 (Cp′), 113.2 (d, J = 5 Hz, Cp′), 108.0 (Cp′), 91.8 (Cp′), 83.5 (d, J = 13 Hz, Cp′), 82.7 (d, J = 13 Hz, Cp′), 82.3 (d, J = 7 Hz, Cp′), 78.7 (Cp′), 60.5 (*C*Me$_3$), 60.0 (d, J = 5 Hz, OCH$_2$), 60.3 (d, J = 5 Hz, OCH$_2$), 30.9 (C*Me*$_3$), 30.4 (C*Me*$_3$), 22.9 (d, J = 35 Hz, PCH$_2$), 20.2 (d, J = 34 Hz, PCH$_2$), 13.5 (Cp′*Me*), 13.3 (Cp′*Me*). IR (cm^{-1}, KBr): 2151 ($\nu_{C\equiv N}$), 1727 ($\nu_{C=O}$). FAB-MS: *m/z* 906 (M − PF_6^-). Anal. Calcd for $C_{50}H_{48}F_6NO_5P_3Ru$: C, 57.15; H, 4.60; N, 1.33. Found: C, 57.21; H, 4.82; N, 1.34. **Major product (2h-I):** ^{1}H NMR (400 MHz): δ 7.90−7.85 (m, 2H, Ph), 7.73−7.29 (m, 13H, Ph), 7.15 (t, 6H, J = 7.3 Hz, OPh), 7.07 (t, 3H, J = 7.3 Hz, OPh), 6.41 (d, 6H, J = 8.5 Hz, OPh), 5.86 (d, 1H, J = 1.7 Hz, Cp′), 5.18 (d, 1H, J = 1.7 Hz, Cp′), 5.27−5.15 (m, 1H, OCH$_2$), 4.34−4.26 (m, 1H, OCH$_2$), 3.15−3.03 (m, 2H, PCH$_2$), 2.44 (s, 3H, Cp′*Me*), 1.75 (s, 9H, CMe$_3$). ^{31}P NMR (162 MHz): δ 128.3 (d, J = 51 Hz), 42.1 (d, J = 51 Hz). **Minor product (2h-II):** ^{1}H NMR (400 MHz): δ 7.84−7.78 (m, 2H, Ph), 7.73−7.29 (m, 19H, Ph, OPh), 7.21 (t, 3H, J = 7.3 Hz, OPh), 6.85 (d, 6H, J = 8.5 Hz, OPh), 5.81 (m, 1H, Cp′), 5.27−5.15 (m, 1H, OCH$_2$), 4.67 (s, 1H, Cp′), 4.18−4.10 (m, 1H, OCH$_2$), 3.35−3.25 (m, 2H, PCH$_2$), 2.56 (d, 3H, J = 8.5 Hz, Cp′*Me*), 1.16 (s, 9H, CMe$_3$). ^{31}P NMR (162 MHz): δ 132.3 (d, J = 53 Hz), 44.3 (d, J = 53 Hz).

[(η^5:η^1-2-Me-4-Bu^t-$C_5H_2CO_2CH_2CH_2PPh_2$)Ru{P(OPh)$_3$}(CNBu^t)][PF_6] (2i-I and 2i-II). IR (cm^{-1}, KBr): 2144 ($\nu_{C\equiv N}$), 1732 ($\nu_{C=O}$). FAB-MS: *m/z* 886 (M − PF_6^-). Anal. Calcd for $C_{48}H_{52}F_6NO_5P_3Ru$: C, 55.92; H, 5.08; N, 1.36. Found: C, 55.72; H, 5.00; N, 1.16. **Major product (2i-II):** ^{1}H NMR (400 MHz): δ 8.02−7.99 (m, 2H, Ph), 7.69−7.48 (m, 8H, Ph), 7.25 (t, 6H,

J = 8.6 Hz, OPh), 7.15 (t, 3H, J = 7.5 Hz, OPh), 6.82 (d, 6H, J = 8.6 Hz, OPh), 5.37 (m, 1H, Cp′), 5.17−5.10 (m, 1H, OCH_2), 4.20 (s, 1H, Cp′), 3.94−3.89 (m, 1H, OCH_2), 3.34−3.29 (m, 1H, PCH_2), 3.19 (dt, 1H, J = 15.4, 4.2 Hz, PCH_2), 2.50 (d, 3H, J = 5.9 Hz, Cp′*Me*), 1.57 (s, 9H, CMe_3), 1.37 (s, 9H, CMe_3). ^{13}C NMR (151 MHz): δ 166.0 (C═O), 152.7 (d, J = 14 Hz, CN), 140.6−121.2 (Ph), 114.2 (Cp′), 92.6 (Cp′), 79.6 (d, J = 4 Hz, Cp′), 79.4 (d, J = 7 Hz, Cp′), 60.7 (d, J = 5 Hz, OCH_2), 60.6 (CMe$_3$), 32.9 (CMe$_3$), 31.1 (C*Me*$_3$), 30.08 (C*Me*$_3$), 21.1 (d, J = 35 Hz, PCH_2), 13.4 (Cp′*Me*). ^{31}P NMR (162 MHz): δ 131.7 (d, J = 55 Hz), 40.0 (d, J = 55 Hz). **Minor product (2i-I):** ^{1}H NMR (600 MHz): δ 6.75 (d, 6H, J = 7.8 Hz, OPh), 2.25 (s, 3H, Cp′*Me*), 1.77 (s, 9H, CMe_3), 1.43 (s, 9H, CMe_3); the signals assignable to the other protons could not be identified due to overlap with those of the major product. ^{31}P NMR (162 MHz): δ 132.5 (d, J = 50 Hz), 38.4 (d, J = 50 Hz).

Reaction of Ruthenium Complexes 1a−f with Phenylacetylene. To a dichloromethane solution (5 mL) of ruthenium complex **1** (0.1 mmol) was added phenylacetylene (0.11 g, 1.0 mmol), and the reaction mixture was refluxed for 48 h. The solvent was evaporated, and the residual oil was washed with diethyl ether several times. The residue was dissolved in dichloromethane and placed on an alumina column. The benzene elution was collected, and the solvent was removed under reduced pressure to give a yellow solid. Yield and diastereoselectivity of the product **4** are given in Table 2. The reaction of **1c** was performed at room temperature for 4 days because no vinylidene complex was formed in the reaction in refluxing dichloromethane.

(η^5:η^1-2,4-Me$_2$-C$_5$H$_2$CO$_2$CH$_2$CH$_2$PPh$_2$)Ru(PPh$_3$)(C≡CPh) (4a-I). ^{1}H NMR (400 MHz): δ 8.02−8.00 (m, 2H, Ph), 7.39−6.79 (m, 26H, Ph), 6.38 (t, 2H, J = 8.3 Hz, Ph), 5.06 (ddd, 1H, J = 19.5, 11.2, 8.3 Hz, OCH_2), 4.52 (d, 1H, J = 2.2 Hz, Cp′), 3.99 (d, 1H, J = 2.2 Hz, Cp′), 3.89−3.84 (m, 1H, OCH_2), 2.67−2.58 (m, 1H, PCH_2), 2.35−2.34 (s, 3H, Cp′*Me*), 2.14 (dt, 1H, J = 14.9, 5.1 Hz, PCH_2), 1.39 (s, 3H, Cp′*Me*). ^{13}C NMR (151 MHz): δ 166.3 (C═O), 142.6−127.4 (Ph), 127.1 (Cp′), 123.0 (Cp′), 110.8 (d, J = 4 Hz, Cp′), 109.9 (d, J = 20 Hz, Ru*C*≡C), 87.0 (d, J = 11 Hz, RuC≡*C*), 84.7 (Cp′), 81.3 (d, J = 9 Hz, Cp′), 58.1 (d, J = 4 Hz, OCH_2), 18.5 (d, J = 25 Hz, PCH_2), 14.2 (Cp′*Me*), 11.8 (Cp′*Me*). ^{31}P NMR (162 MHz): δ 47.5 (d, J = 31 Hz), 35.3 (d, J = 31 Hz). IR (cm^{-1}, KBr): 2076 ($\nu_{C\equiv C}$), 1704 ($\nu_{C=O}$). FAB-MS: *m/z* 814 (M$^+$). Anal. Calcd for $C_{48}H_{42}O_2P_2$-Ru: C, 70.84; H, 5.20. Found: C, 70.62; H, 5.27.

(η^5:η^1-2-Me-4-Ph-C$_5$H$_2$CO$_2$CH$_2$CH$_2$PPh$_2$)Ru(PPh$_3$)(C≡CPh) (4b). ^{1}H NMR (400 MHz): δ 7.80−7.76 (m, 2H, Ph), 7.66−7.64 (m, 2H, Ph), 7.48−6.77 (m, 27H, Ph), 6.33 (t, 2H, J = 8.5 Hz, Ph), 6.26 (d, 2H, J = 7.3 Hz, Ph), 5.16−5.06 (m, 1H, OCH_2), 5.09 (s, 1H, Cp′), 4.50 (s, 1H, Cp′), 3.96 (dt, 1H, J = 10.3, 5.1 Hz, OCH_2), 2.74−2.66 (m, 1H, CH_2P), 2.20 (dt, 1H, J = 14.6, 5.1 Hz, PCH_2), 1.50 (s, 3H, Cp′*Me*). ^{13}C NMR (100 MHz): δ 166.2 (C═O), 142.3−127.0 (Ph), 122.7 (Cp′), 113.1 (d, J = 5 Hz, Cp′), 110.8 (Ru*C*≡C or Cp′), 110.1-(Ru*C*≡C or Cp′), 86.2 (Cp′), 84.9 (d, J = 13 Hz, RuC≡*C*), 78.3 (d, J = 8 Hz, Cp′), 58.3 (d, J = 4 Hz, OCH_2), 20.0 (d, J = 26 Hz, PCH_2), 12.1 (Cp′*Me*). ^{31}P NMR (162 MHz): δ 47.8 (d, J = 31 Hz), 36.2 (d, J = 31 Hz). IR (cm^{-1}, KBr): 2080 ($\nu_{C\equiv C}$), 1708 ($\nu_{C=O}$). FAB-MS: *m/z* 876 (M$^+$). Anal. Calcd for $C_{53}H_{44}O_2P_2Ru$: C, 72.59; H, 5.17. Found: C, 72.39; H, 4.88.

(η^5:η^1-2-Me-4-Bu^t-C$_5$H$_2$CO$_2$CH$_2$CH$_2$PPh$_2$)Ru(PPh$_3$)(C≡CPh) (4c-I). ^{1}H NMR (400 MHz): δ 8.08 (t, 3H, J = 8.4 Hz, Ph), 7.38−7.25 (m, 16H, Ph), 7.04 (t, 2H, J = 7.5 Hz, Ph), 6.99 (t, 2H, J = 7.5 Hz, Ph), 6.91 (t, 1H, J = 7.1 Hz, Ph), 6.81 (d, 2H, J = 8.4 Hz, Ph), 6.73 (t, 2H, J = 7.5 Hz, Ph), 6.49 (t, 2H, J = 8.4 Hz, Ph), 5.07 (ddd, 1H, J = 19.0, 11.2, 7.9 Hz, OCH_2), 4.77 (s, 1H, Cp′), 3.72 (s, 1H, Cp′), 3.68−3.64 (m, 1H, OCH_2), 3.02−2.96 (m, 1H, PCH_2), 2.14 (dt, 1H, J = 14.5, 4.8 Hz, PCH_2), 1.63 (s, 3H, Cp′*Me*), 1.59 (s, 9H, CMe_3). ^{13}C NMR (151 MHz): δ 167.8 (C═O), 142.8−127.4 (Ph), 127.2 (d, J = 10 Hz, Cp′), 122.8 (Cp′), 114.3 (d, J = 11 Hz, Ru*C*≡C), 105.8 (Cp′), 86.9 (d, J = 11 Hz, RuC≡*C*), 86.4 (Cp′), 71.7 (d, J = 10 Hz, Cp′), 58.8 (OCH_2), 33.0 (CMe$_3$), 30.3 (C*Me*$_3$), 19.5 (d, J = 26 Hz, PCH_2), 12.3 (Cp′*Me*). ^{31}P NMR (162 MHz): δ 44.4 (d, J = 29 Hz), 21.7 (d, J = 29 Hz). IR (cm^{-1}, KBr): 2081 ($\nu_{C\equiv C}$), 1713 ($\nu_{C=O}$). FAB-MS: *m/z* 856 (M$^+$). Anal. Calcd for $C_{51}H_{48}O_2P_2Ru$: C, 71.56; H, 5.65. Found: C, 71.56; H, 5.65.

(η^5:η^1-2,4-Me$_2$-C$_5$H$_2$CO$_2$CH$_2$CH$_2$PPh$_2$)Ru(PMe$_3$)(C≡CPh) (4d). IR (cm^{-1}, KBr): 2076 ($\nu_{C\equiv C}$), 1697 ($\nu_{C=O}$). FAB-MS: *m/z* 628 (M$^+$). Anal. Calcd for $C_{33}H_{36}O_2P_2Ru$: C, 63.15; H, 5.78. Found: C, 63.14; H, 5.68. **Major product (4d-II):** ^{1}H NMR (600 MHz): δ 7.65 (t, 2H, J = 8.1 Hz, Ph), 7.52−7.48 (m, 3H, Ph), 7.31 (d, 2H, J = 8.1 Hz, Ph), 7.26−7.15 (m, 6H, Ph), 7.04 (t, 1H, J = 7.3 Hz, Ph), 5.02−4.95 (m, 1H, OCH_2), 4.77 (s, 1H, Cp′), 4.58 (s, 1H, Cp′), 3.79−3.74 (m, 1H, OCH_2), 3.31−3.24 (m, 1H, PCH_2), 2.34 (s, 3H, Cp′*Me*), 2.27−2.22 (m, 1H, PCH_2), 2.22 (s, 3H, Cp′*Me*), 1.00 (d, 9H, J = 9.2 Hz, PMe_3). ^{13}C NMR (151 MHz): δ 164.7 (C═O), 142.2−127.5 (Ph), 123.4 (Ru*C*≡C), 114.4 (Cp′), 105.6 (RuC≡*C*), 94.8 (Cp′), 89.2 (Cp′), 84.5 (d, J = 10 Hz, Cp′), 79.5 (d, J = 9 Hz, Cp′), 58.3 (d, J = 4 Hz, OCH_2), 22.1 (d, J = 34 Hz, PCH_2), 20.6 (d, J = 30 Hz, PMe_3), 14.2 (Cp′*Me*), 13.6 (Cp′*Me*). ^{31}P NMR (162 MHz): 45.1 (d, J = 39 Hz), 9.7 (d, J = 39 Hz). **Minor product (4d-I):** ^{1}H NMR (600 MHz): δ 7.91−7.88 (m, 2H, Ph), 7.74−7.73 (m, 1H, Ph), 7.41−6.95 (m, 12H, Ph), 5.07 (ddd, 1H, J = 20.1, 10.7, 7.1 Hz, OCH_2), 4.61 (s, 1H, Cp′), 4.53 (s, 1H, Cp′), 3.87−3.82 (m, 1H, OCH_2), 2.76−2.64 (m, 2H, PCH_2), 2.35 (d, 3H, J = 3.0 Hz, Cp′*Me*), 2.30 (d, 3H, J = 1.6 Hz, Cp′*Me*), 0.98 (d, 9H, J = 9.1 Hz, PMe_3). ^{31}P NMR (162 MHz): δ 38.2 (d, J = 36 Hz), 9.5 (d, J = 36 Hz).

(η^5:η^1-2-Me-4-Ph-C$_5$H$_2$CO$_2$CH$_2$CH$_2$PPh$_2$)Ru(PMe$_3$)(C≡CPh) (4e). IR (cm^{-1}, KBr): 2084 ($\nu_{C\equiv C}$), 1704 ($\nu_{C=O}$). FAB-MS: *m/z* 690 (M$^+$). Anal. Calcd for $C_{38}H_{38}O_2P_2Ru$: C, 66.17; H, 5.55. Found: C, 66.44; H, 5.35. **Major product (4e-II):** ^{1}H NMR (600 MHz): δ 7.66−6.69 (m, 20H, Ph), 5.37 (s, 1H, Cp′), 5.17 (s, 1H, Cp′), 5.10−5.03 (m, 1H, OCH_2), 3.95−3.90 (m, 1H, OCH_2), 3.34−3.27 (m, 1H, PCH_2), 2.50 (s, 3H, Cp′*Me*), 2.27 (dt, 1H, J = 14.6, 4.9 Hz, PCH_2), 0.71 (d, 9H, J = 9.6 Hz, PMe_3). ^{13}C NMR (151 MHz): 164.7 (C═O), 142.0−125.0 (Ph), 123.5 (Ru≡*C*C), 114.7 (Cp′), 105.7 (RuC≡*C*), 97.2 (Cp′), 86.2 (Cp′), 80.8 (d, J = 7 Hz, Cp′), 79.7 (d, J = 11 Hz, Cp′), 58.5 (d, J = 3 Hz, OCH_2), 21.7 (d, J = 35 Hz, PCH_2), 19.5 (d, J = 31 Hz, PMe_3), 13.9 (Cp′*Me*). ^{31}P NMR (162 MHz): 43.6 (d, J = 38 Hz), 9.5 (d, J = 38 Hz). **Minor product (4e-I):** ^{1}H NMR (600 MHz): δ 7.66−6.69 (m, 20H, Ph), 5.19 (s, 1H, Cp′), 5.09 (s, 1H, Cp′), 5.10−5.03 (m, 1H, OCH_2), 4.05−4.00 (m, 1H, OCH_2), 2.79−2.69 (m, 2H, PCH_2), 2.42 (d, 3H, J = 2.5 Hz, Cp′*Me*), 1.03 (d, 9H, J = 9.1 Hz, PMe_3). ^{31}P NMR (162 MHz): δ 39.1 (d, J = 36 Hz), 10.6 (d, J = 36 Hz).

(η^5:η^1-2-Me-4-Bu^t-C$_5$H$_2$CO$_2$CH$_2$CH$_2$PPh$_2$)Ru(PMe$_3$)(C≡CPh) (4f). IR (cm^{-1}, KBr): 2080 ($\nu_{C\equiv C}$), 1714 ($\nu_{C=O}$). FAB-MS: *m/z* 670 (M$^+$). Anal. Calcd for $C_{36}H_{42}O_2P_2Ru$: C, 64.56; H, 6.32. Found: C, 65.02; H, 6.26. **Major product (4f-I):** ^{1}H NMR (400 MHz): δ 8.02−7.97 (m, 2H, Ph), 7.50−6.92 (m, 13H, Ph), 5.04−4.94 (m, 1H, OCH_2), 4.87 (s, 1H, Cp′), 4.53 (s, 1H, Cp′), 3.64−3.57 (m, 1H, OCH_2), 2.82−2.74 (m, 1H, PCH_2), 2.53 (dt, 1H, J = 14.1, 4.4 Hz, PCH_2), 2.37 (s, 3H, Cp′*Me*), 1.54 (s, 9H, CMe_3), 0.95 (d, 9H, J = 9.1 Hz, PMe_3). ^{13}C NMR (151 MHz): δ 167.7 (C═O), 143.0−127.3 (Ph), 123.4 (Ru*C*≡C), 115.3 (Cp′), 110.7 (RuC≡*C*), 103.9 (Cp′), 87.2 (Cp′), 78.2 (d, J = 10 Hz, Cp′), 73.9 (d, J = 8 Hz, Cp′), 58.5 (d, J = 3 Hz, OCH_2), 32.5 (CMe$_3$), 30.7 (C*Me*$_3$), 22.8 (d, J = 31 Hz, PCH_2), 19.0 (d, J = 31 Hz, PMe_3), 13.7 (Cp′*Me*). ^{31}P NMR (162 MHz): δ 35.9 (d, J = 35 Hz), 9.0 (d, J = 35 Hz). **Minor product (4f-II):** ^{1}H NMR (400 MHz): δ 7.85−7.79 (m, 2H, Ph), 7.50−6.92 (m, 13H, Ph), 5.04−4.94 (m, 1H, OCH_2), 4.87 (s, 1H, Cp′), 4.59 (s, 1H, Cp′), 3.79−3.73 (m, 1H, OCH_2), 3.45−3.37 (m, 1H, PCH_2), 2.39 (s, 3H, Cp′*Me*), 2.20 (dt, 1H, J = 14.4, 4.6 Hz, PCH_2), 1.37 (s, 9H, CMe_3), 1.04 (d, 9H, J = 9.0 Hz, PMe_3). ^{31}P NMR (162 MHz): δ 45.41 (d, J = 36 Hz), 7.6 (d, J = 36 Hz).

X-ray Diffraction Analyses of Complexes 2c-I, 4a-I, and 4c-I. Crystals suitable for X-ray diffraction were mounted

Table 3. Summary of Crystallographic Data for Complexes 2c-I, 4a-I, and 4c-I

	2c-I	**4a-I**·0.5$CHCl_3$	**4c-I**·CH_2Cl_2
empirical formula	$C_{48}H_{52}F_6NO_2P_3Ru$	$C_{48.5}H_{42.5}Cl_{1.5}O_2P_2Ru$	$C_{52}H_{50}Cl_2O_2P_2Ru$
fw	982.93	873,57	982.93
cryst dimens/mm	0.30 × 0.20 × 0.05	0.50 × 0.25 × 0.05	0.25 × 0.20 × 0.15
cryst syst	monoclinic	triclinic	monoclinic
lattice params			
a/Å	13.739(6)	12.584(6)	9.875(2)
b/Å	18.886(6)	19.703(9)	21.578(2)
c/Å	17.871(5)	9.045(7)	21.305(2)
α/deg		98.03(6)	
β/deg	93.53(3)	104.57(3)	101.92(1)
γ/deg		72.12(4)	
V/Å^3	4628(2)	2060(2)	4441(1)
space group	$P2_1/n$ (# 14)	$P\bar{1}$ (# 2)	$P2_1/c$ (# 14)
Z value	4	2	4
D_{calcd}/g cm^{-3}	1.411	1.408	1.407
F(000)	2024	898	1944
μ(Mo Kα)/cm^{-1}	5.05	5.94	5.86
no. reflns measd			
total	11 450	9954	9100
unique	11 106 (R_{int} = 0.160)	9518 (R_{int} = 0.094)	8844 (R_{int} = 0.160)
no. observations	5661 ($I > 2.0\sigma(I)$)	7843 ($I > 2.0\sigma(I)$)	5016 ($I > 2.0\sigma(I)$)
no. params	602	554	582
residuals: R1; wR2	0.054; 0.114	0.047; 0.082	0.065; 0.130
GOF	1.098	1.186	1.177
peak, hole/e Å^{-3}	0.86, −1.02	0.92, −1.51	1.25, −1.05

on a glass fiber with epoxy resin. All measurements were performed on a Rigaku AFC7R or AFC5R automated four-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). A summary of crystallographic data is given in Table 3. Additional information on the collection of the data and the refinement of the structures is available as Supporting Information.

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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.

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