# **Preparation of Ruthenium Azirinyl Complexes and Reversed Regiospecificity of the Carbonyl Insertion** Reaction

Yih-Hsing Lo, Sheng-Cheng Hsu, Shou-Ling Huang, Ying-Chih Lin,\* Yi-Hong Liu, and Yu Wang

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China

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Electrophilic addition of organic halides to [Ru]CN (1; [Ru] =  $Cp(PPh_3)_2Ru$ ) gave the cationic isocyanide complexes { $[Ru]CNCH_2R$ }X (R = CN, **2a**; R = CH=CH<sub>2</sub>, **2b**; R = Ph, **2c**), which reacted with base (*n*-Bu<sub>4</sub>NOH or *n*-Bu<sub>4</sub>NF) to give the three-membered-ring azirinyl complexes. For the azirinyl complex with a phenyl group **3c**, three isomers, assigned as ruthenium 2H- and 1H-azirinyl complexes, are observed at -20 °C. Reaction of the methyl isocyanoacetate complex  $\{[Ru]C \equiv NCH_2COOMe\}X$  (2d) with *n*-Bu<sub>4</sub>NOH causes hydrolysis of the ester group to give the ruthenium oxazolone complex 4d. The insertion of the C=O group of acetone, aldehyde, ester, and amide into the C-C bond of the three-membered azirinyl ring of 3a-c yields a variety of five-membered oxazolinyl complexes 5-7. The regiospecificity of the insertion differs from that observed in the photochemically induced carbonyl insertion in the organic azirine system. The diastereoselectivity in the formation of 5-7 is controlled by steric effects. In the formation of the pentamethylcyclopentadienyl oxazolinyl ruthenium complex  $7a^*$ , the intermediate  $8a^*$  is isolated before cyclization. Molecular structures of **7a**<sup>\*</sup> and **8a**<sup>\*</sup> have been determined by single-crystal X-ray diffraction analysis. Treatment of **7** with hydride gave [Ru]CN and alcohol.

## Introduction

Azirine (azacyclopropene) has attracted much attention from the perspective of its strained molecular structure and unique reactivity. The synthetic and theoretical chemistry of azirine have been extensively investigated, and a number of general reviews on azirines have appeared.<sup>1</sup> The ring system occurs naturally with dysidazirine,<sup>2</sup> found as a constituent of marine sponges, and azirinomycin, an antibiotic isolated from streptomyces aureus cultures.<sup>3</sup> Due to the asymmetry of the azirine there are two isomers, referred to as 1*H*- and 2*H*-azirine. The former, known only as a transient intermediate, represents a cyclic conjugated system with four  $\pi$ -electrons. The 2*H*-azirine, however,

shows interesting chemical behavior, and many reactions of the compound can be used in the synthesis of heterocyclic compounds. The effect of ring strain upon chemical reactivity and the potential for their derivatives to act as precursors to more sophisticated heterocyclic molecules have stimulated interest in these nitrogen-containing heterocycles. The total ring-strain energy of 2H-azirine has been estimated at about 48 kcal/mol, mostly owing to deformation of normal bond angles between the atoms of the ring,<sup>4</sup> although lower values of 44.6 and 46.7 kcal/mol have recently been reported.<sup>5</sup> The stabilities of these heterocycles are attributable to the collective results of bond shortening and angle compression as well as the presence of the electron-rich nitrogen atom. A shorter C-N bond and a longer C-C bond revealed by single-crystal X-ray data of 2*H*-azirines may be a sign of polarization toward the more electronegative nitrogen atom.<sup>6</sup> The corresponding values for the isoelectric cyclopropene ring are about 10 kcal/mol higher than for 2*H*-azirine at the same levels of theory. Calculations showed that the azirinyl cation exhibited aromatic properties.<sup>7</sup>

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A number of general methods<sup>8</sup> are available for the synthesis of organic 2H-azirines. These include the modified Neber reaction, thermolysis and photolysis of vinyl azide and isoxazoles, and thermolysis of oxazaphospholines. Strained azirine ring compounds show a considerable variety of photochemical behavior, and many of the reactions can be put to good use in the synthesis of heterocyclic compounds.<sup>9</sup> It is known that photochemically induced reaction<sup>10</sup> of azirines with ketone or aldehyde leads to isolation of oxazolines, whose metal complexes have been extensively used in metal-catalyzed enantioselective synthesis.<sup>11</sup> However, metal complexes containing azirinyl ligands are rare, possibly due to the lack of suitable synthetic methods. We previously described a cyclization reaction by deprotonation of a cationic ruthenium vinylidene complex containing a  $-CH_2R$  group at  $C_\beta$  of the vinylidene ligand to give a metal complex containing a strained cyclopropenyl ligand.<sup>12</sup> Using this strategy, we reported the preparation of several ruthenium cyclopropenyl complexes containing various substituents. This reaction also results in formation of a stereogenic carbon center in the three-membered ring. These features render this cyclization process potentially useful for organic synthesis.<sup>13</sup> Therefore, we set out to explore deprotonation reactions of the cationic ruthenium isocyanide [Ru]C≡ NCH<sub>2</sub>R<sup>+</sup> system. The expected three-membered azirinyl complex is obtained and has been identified by spectroscopic methods. In the presence of ketone, aldehyde, or ester, an unprecedented facile insertion reaction of a carbonyl group of ketone, aldehyde, or ester into the C-C bond of the azirinyl ring obtained from ruthenium isocyanides is observed. Herein we report the preparation of the cationic ruthenium isocyanide complexes [Cp(LL')RuCNCH<sub>2</sub>R]X and subsequent deprotonation reaction and insertion of a carbonyl group into the azirinyl ligand.14

## **Results and Discussion**

Synthesis of Isocyanide Complexes by Alkylation. Cationic isocyanide complexes are usually prepared by direct ligand exchange.<sup>15</sup> However, many free isocyanides of the type CNCH<sub>2</sub>R are not commercially available. Therefore, other methods for the synthesis of isocyanide complexes are desirable. The chemistry of the coordinated cyano ligand has been extensively investigated in the past,<sup>16</sup> and it is known that the nitrogen atom of the cyano ligand is a good nucleophile. Thus, it is reasonable to propose the preparation of isocyanide complexes by alkylation reactions of transition-metal cyanide complexes with carbon electrophiles.<sup>17</sup> We found that this preparative method is convenient to introduce alkyl or aryl groups to the ruthenium-coordinated cyanide ligand using various organic halides.

Treatment of 1 with excess bromoacetonitrile in CHCl<sub>3</sub> at reflux temperature afforded a green solution. Evaporation of the solvent under reduced pressure gave a green oil, which was then dissolved in a minimum amount of CH<sub>2</sub>Cl<sub>2</sub>. Addition of this solution dropwise into vigorously stirred Et<sub>2</sub>O caused the pale green solids to precipitate out. The solid was collected by filtration and washed with  $Et_2O$  to afford {[Ru]C=NCH<sub>2</sub>CN}Br  $(2a; [Ru] = Cp(PPh_3)_2Ru)$  with 75% yield. Similarly, preparations of complexes [Ru]CNCH<sub>2</sub>R<sup>+</sup> (R = CH=CH<sub>2</sub>, **2b**;  $R = C_6H_5$ , **2c**;  $R = COOCH_3$ , **2d**) have all been achieved with good yields. Previously more than 40 equiv of allyl bromide and long reaction times were employed for preparing **2b** and the isolated yield was 45%. We use 5 equiv of allyl iodide, instead of allyl bromide, for the preparation of **2b** at room temperature, and in 3 h the product is isolated with 92% yield. Use of CHCl<sub>3</sub> as a solvent usually achieved high yield for the synthesis of these ruthenium isocyanide complexes. Use of iodide reagents effectively increases the reaction rate and the yield is also improved, except for the preparation of **2a**.

The <sup>1</sup>H NMR spectrum of 2a shows the expected methylene peak at  $\delta$  5.51. In the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, the singlet resonance at  $\delta$  45.4 is assigned to the PPh<sub>3</sub> ligand. In the <sup>1</sup>H NMR spectrum of **2d** in CDCl<sub>3</sub>, the singlet resonance at  $\delta$  4.92 is assigned to the methylene group of the isocyanide ligand, slightly shifted from that of **2a**. Two singlet resonances at  $\delta$  4.76 and 3.60 are assigned to the Cp and methyl groups, respectively. In the <sup>13</sup>C NMR spectrum of **2d** in CDCl<sub>3</sub>, the most characteristic spectroscopic data consist of a singlet resonance at  $\delta$  165.4 assigned to the carbonyl carbon, and the triplet resonance at  $\delta$  158.6 with  ${}^{2}J_{\rm C-P}$ = 20.2 Hz is assigned to the ruthenium-bonded isocyanide carbon, symbolized here as  $C_{\alpha}$ . The methyl and methylene resonances of the isocyanide ligand appear as two singlets at  $\delta$  52.5 and 47.8, respectively. The <sup>31</sup>P

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NMR spectrum of **2d** displays a singlet resonance at  $\delta$  46.0 in CDCl<sub>3</sub>. The FAB mass spectrum shows the parent peak at m/z 790 as well as peaks at m/z 528 and 429 due to loss of a PPh<sub>3</sub> and both PPh<sub>3</sub> and isocyanide ligand, respectively. Mass spectra of other ruthenium isocyanide complexes display the same fragmentation pattern.

Ruthenium isocyanide complexes with pentamethylcyclopentadienyl and dppp ((diphenylphosphino)propane) ligands were also prepared. Treatment of [Ru\*]CN ([Ru\*] = ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(dppp)Ru, 1\*) with PhCH<sub>2</sub>Br affords the cationic isocyanide complex {[Ru\*]CNCH<sub>2</sub>Ph}Br (**2c**\*) in high yield. In the <sup>13</sup>C NMR spectrum of **2c**\*, the triplet resonance at  $\delta$  160.65 with  $J_{P-C} = 19.4$  Hz is assigned to C<sub>a</sub>. The C<sub>a</sub> resonance of the previously reported ruthenium isocyanide compound Cp\*Ru(CN)-(CN<sup>t</sup>Bu)(Ppyl<sub>3</sub>), (Ppyl<sub>3</sub> = tripyrrolylphosphine) was found at  $\delta$  155.6 as a doublet with  $J_{P-C} = 25.8$  Hz in the <sup>13</sup>C NMR spectrum.<sup>18</sup>

Reaction of Isocyanide Complexes 2a,b with **Base.** The cationic character of complexes **2** is expected to enhance the acidity of the methylene proton of the isocyanide ligand. An additional terminal electronwithdrawing CN group in 2a should cause deprotonation to occur readily. It is therefore not surprising to observe high-yield formation of the thermally unstable three-membered-ring azirinyl complex 3a (see Scheme 1) when 2a in  $CH_2Cl_2$  is treated with a solution of *n*-Bu<sub>4</sub>NOH in methanol at 0 °C. MeONa in MeOH could also be used as a base for this reaction, but the reaction gives a lower yield of **3a**. Complex **3a** decomposes to **1** and some unidentifiable products at room temperature and is characterized spectroscopically. The singlet <sup>31</sup>P NMR resonance at  $\delta$  45.4 for **2a** is converted to two doublet resonances at  $\delta$  49.1 and 48.7 with  $J_{P-P} = 34.8$ Hz, clearly indicating the formation of an azirinyl ring containing a stereogenic carbon center. In the <sup>13</sup>C NMR

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spectrum of **3a**, the triplet resonance at  $\delta$  184.3 with  $J_{\rm C-P} = 19.9$  Hz is assigned to  $C_{\alpha}$ . The <sup>1</sup>H NMR resonance of the azirinyl ring proton appears at  $\delta$  2.98, similar to that of other organic azirine systems.<sup>19</sup> In the 2D HMQC NMR spectrum of **3a**, this resonance correlates to the <sup>13</sup>C resonance at  $\delta$  11.3 assignable to the sp<sup>3</sup> carbon atom of the azirinyl ligand. These data establish the structure of **3a**. Addition of protic acid to **3a** opens the three-membered ring, generating **2a**.

Similarly, deprotonation of {[Ru]CNCH<sub>2</sub>CH=CH<sub>2</sub>}I (**2b**) by *n*-Bu<sub>4</sub>NF at 0 °C in  $CH_2Cl_2$  affords the azirinyl complex 3b in 88% yield. Use of DBU or n-Bu<sub>4</sub>NOH/ MeOH, instead of *n*-Bu<sub>4</sub>NF, gives several unidentifiable complexes along with **3b** as a minor product. In the <sup>31</sup>P NMR spectrum of **3b** the two-doublet pattern, i.e., resonances at  $\delta$  52.0 and 48.8 with  $J_{P-P} = 34.8$  Hz, is consistent with the presence of a stereogenic center. In the <sup>1</sup>H NMR spectrum of **3b** three multiplet resonances at  $\delta$  5.73, 5.26, and 5.21 are assigned to three protons of the vinyl group in the three-membered ring. The ddd coupling pattern of the resonance at  $\delta$  5.73 assignable to the internal =CH, as compared to the ddt coupling pattern of the resonance at  $\delta$  5.59 in **2b**, clearly discloses the presence of a neighboring CH group of the ring resulting from the deprotonation reaction. The doublet resonance with relative integration of one proton at  $\delta$ 2.76 is assigned to the proton on the azirinvl ring. Again addition of protic acid to 3b yields 2b.

In contrast to the metal vinylidene system with a bent structure at  $C_{\beta}$ , the isocyanide ligand is linear. Therefore, the deprotonation step should yield a bent transient zwitterionic nitrile ylide (see Scheme 2) with an anionic charge most likely located at the methyne carbon atom of the isocyanide ligand, thus facilitating formation of the three-membered azirinyl ring.<sup>20</sup> This reaction is analogous to the facile deprotonation-induced cyclopropenation of the cationic ruthenium vinylidene system. In the vinylidene complex, the bent structure at  $C_{\beta}$  could assist formation of the cyclopropenyl ligand.<sup>21</sup> It has been stressed that nitrile ylides, generated from the photolysis of 2*H*-azirines, may be classified as nitrilium betaines, a class of 1,3-dipoles containing a

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Figure 1.  $2D^{31}P$  NMR spectrum of complex 3c, revealing the presence of three isomers.

central nitrogen and a  $\pi$  bond orthogonal to the  $4\pi$  allyl system. While metal to carbon back-bonding is substantial, the bonding situation of the metal-isocyanide linkage is probably more adequately represented by bending of the coordinated CNR unit.<sup>22</sup>

Three Isomers of the Phenylazirinyl Complex. Deprotonation of  $\{[Ru]CNCH_2Ph\}Br(2c)$  in  $CH_2Cl_2$  by n-Bu<sub>4</sub>NOH at 0 °C also affords, in high yield, the thermally unstable azirinyl complex 3c along with [Ru]CN (1) as a minor product (ca. 5%). Use of other bases such as DBU and n-Bu<sub>4</sub>NF in THF also gave similar products, but with lower yield. The <sup>31</sup>P NMR spectrum of 3c at -20 °C displays three sets of doublet of doublets patterns at  $\delta$  51.98, 48.82,  $\delta$  51.89, 49.72, and  $\delta$  51.17, 50.15 in a ratio of approximately 2:2:3. The 2D<sup>31</sup>P NMR COSY spectrum (Figure 1) reveals coupling pairs corroborating the presence of stereogenic centers of all three isomers. At -40 °C only one isomer is detected. These could possibly be due to the fluxional behavior of the three isomers 3c-I, 3c-II, and 3c-III of the azirinyl complex, i.e., 1H-azirinyl and two 2Hazirinyl complexes (Scheme 1), with one of them being thermodynamically more stable. The <sup>1</sup>H NMR spectrum at -20 °C displaying three Cp singlet resonances at  $\delta$ 4.59, 4.58, and 4.57 also in a ratio of 3:2:2, respectively, is consistent with the <sup>31</sup>P NMR data. Two <sup>1</sup>H NMR resonances at  $\delta$  4.89 and 4.71 are assigned to the CH groups, and the broad resonance at  $\delta$  3.23 is assigned to the NH group. Addition of  $D_2O$  to the solution of 3cat -20 °C causes immediate disappearance of the resonance at  $\delta$  3.23, confirming this assignment. This is followed by slow vanishing of the resonances at  $\delta$  4.89 and 4.71, indicating the presence of exchange processes between these three isomers. At -29 °C the species with  $^{31}\mathrm{P}$  resonances at  $\delta$  51.17 and 50.15 and  $^{1}\mathrm{H}$  resonance at  $\delta$  3.23 disappears first. Then at -40 °C only one isomer with  $^{31}\mathrm{P}$  resonances at  $\delta$  51.89 and 49.72 and <sup>1</sup>H resonance at  $\delta$  4.71 was observed. Attempts to obtain

<sup>13</sup>C NMR data caused extensive decomposition of the product. On the basis of these NMR data and spectroscopic data of **3a**,**b** we believe that **3c-I** (Scheme 1) is probably the most stable isomer among the three. Reaction of  $\{[Ru]CNCH_2C_6H_4CN\}Br$  (2c') with base vielded the corresponding azirinyl complex 3c', which also shows three isomeric forms in a similar ratio by NMR. It seems that the presence of an aromatic group at  $C_{\nu}$  (the methylene group) of the isocyanide ligand is required in order to see three azirinyl isomers. Even though free 1*H*-azirine is considered as the least stable isomer in a pure organic system, the three-membered ring of the metalated 1*H*-azirine at one of the  $sp^2$ carbons (3c-II) could significantly be stabilized by participation of metal d orbirals, thus making 3c-III the least stable among the three.<sup>23</sup>

Hydrolysis of the Isocyanide Complex with an **Ester Group.** Treatment of  $\{[Ru]C \equiv NCH_2CO_2CH_3\}I$ , (2d) in acetone with *n*-Bu<sub>4</sub>NOH affords the orange oxazolone complex 4d in 72% yield (Scheme 1). Hydrolysis of the ester group accounts for the formation of 4d. Lacking a stereogenic carbon atom, complex 4d displays a singlet resonance at  $\delta$  50.5 in the <sup>31</sup>P NMR spectrum, and in the <sup>1</sup>H NMR spectrum the 5:2 ratio for the two singlet resonances at  $\delta$  4.69 and 4.13, assignable to the Cp and CH<sub>2</sub> groups, is consistent with the formula. In the FAB mass spectrum, a parent peak at m/z 776.2 attributed to  $(M + 1)^+$  is observed.<sup>24</sup> We previously reported the deprotonation reaction of a cationic vinylidene complex containing a methyl ester group at  $C_{\gamma}$ , i.e. [Ru]=C=C(Ph)CH<sub>2</sub>CO<sub>2</sub>R<sup>+</sup>, leading to a thermodynamically stable neutral five-membered methoxyfuryl complex with no hydrolysis of the ester group. The three-membered-ring cyclopropenyl complex was observed as an intermediate at the initial stage of the deprotonation reaction of the vinylidene complex. However, in the reaction of **2d** with base leading to **4d**, no azirinyl complex with an ester substituent was observed during the reaction.

Transition-metal-induced reactions of azirine have been reported in a few cases. Initial 1,3-bond cleavage and generation of a nitrene—iron carbonyl complex as an intermediate was proposed in the reaction of azirine with diiron nonacarbonyls to give diimine complexes and urea diiron complexes.<sup>25</sup> Cycloaddition of alkynes

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<sup>(23)</sup> MO calculations show 1*H*-azirine to be approximately 30 kcal less stable than 2*H*-azirine: Hopkinson, A. C.; Lien, M. A.; Yates, K.; Csizmadia, J. G. Intern. J. Quantum Chem. **1977**, *12*, 355. (Phthalimidonitrene, generated by lead tetraacetate oxidation of *N*-aminophthalimide, reacts with acetylenes to give the 1-azirines. This work provides good evidence of the probable intermediate for the formation of a 2-azirine system: Gilchrist, T. L.; Gymer, G. E.; Rees, C. W. J. *Chem. Soc., Chem. Commun.* **1971**, 1519–1520. Gilchrist, T. L.; Gymer, G. E.; Rees, C. W. J. Chem. Soc., Perkin Trans. *1* **1973**, 555–561.) We have used the Spartan semiempirical method to calculate the relative energies of three simplified isomers Cp(PH<sub>3</sub>)<sub>2</sub>Ru(CNCHPh) (**3c'-1, 3c'-II**, **3c'-III**) and found that **3c-I** is the most stable one among the possible isomers.

<sup>(24) (</sup>a) Hoshimoto, S.; Matsunaga, H.; Wada, M.; Kunieda, T. Chem. Pharm. Bull. 2002, 50, 435–438. (b) Sebahar, H. L.; Yoshida, K.; Hegedus, L. S. J. Org. Chem. 2002, 67, 3788–3795. (c) Dialer, H.; Schumann, S.; Polborn, K.; Steglich, W.; Beck, W. Eur. J. Inorg. Chem. 2001, 1675–1679. (d) Umetani, S.; Kawase, Y.; Le, Q. T. H.; Matsui, M. Dalton 2000, 2787–2791. (e) Prem, M.; Bauer, W.; Polborn, K.; Beck, W. Z. Naturforsch., B 1998, 53, 965–970.

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Photochemical Insertion Reaction of Organic Azirine



with 2-phenylazirines in the presence of  $Mo(CO)_6$  appears to proceed by an initial [2 + 2] cycloaddition followed by a ring-opening reaction to give pyrrole derivatives.<sup>26</sup>

Insertion of a Carbonyl Group into the Azirinyl Ring. The reaction of 2a with n-Bu<sub>4</sub>NOH/MeOH in acetone, instead of CH<sub>2</sub>Cl<sub>2</sub>, yields a different product, identified as the oxazolinyl complex 5a (Scheme 3). The reaction of **3a** with acetone also gave **5a**. For the latter species, insertion of the carbonyl group of acetone into the C-C bond of the azirinyl ring with C-C bond formation occurring at the sp<sup>3</sup> carbon of the azirinyl ring satisfactorily accounts for the formation of 5a. Complex 5a with a five-membered-ring ligand is more stable than that of **3a**. The <sup>31</sup>P NMR spectrum of **5a** displays two doublet resonances at  $\delta$  50.0 and 51.0 with  $J_{\rm P-P}=34.5$ Hz, consistent with the presence of a stereogenic carbon center in the oxazolinyl ring. In the <sup>13</sup>C NMR spectrum of **5a**, the triplet resonance of  $C_{\alpha}$  at  $\delta$  197.6 with  $J_{C-P}$ = 18.8 Hz is in the vicinity of the corresponding resonance in 3a. The reaction of methyl ethyl ketone with **3a** gave **5b** in 79% yield. Two diastereoisomers in a ratio of 5:4 are observed in the <sup>31</sup>P NMR data, and after 30 days at room temperature the minor species decreases to give a ratio of 2:1. It is clear that the steric bulk controls the stereoselectivity. The regiochemistry of ketone insertion, however, is not directly revealed by the spectroscopic data mentioned above. Fortunately, the same insertion also takes place for organic aldehyde. We carried out the reaction of 3a with PhCHO in chloroform. This reaction requires mild heating and results in a mixture of diastereoisomers of 5c in a 5:1

ratio. In 3 days at room temperature, the minor isomer in solution turned into the major one. This transformation may indicate the presence of a dynamic equilibrium between the azirinyl and the oxazolinyl rings. In the <sup>1</sup>H NMR spectrum of the crude product, two pairs of two-doublet resonances at  $\delta$  4.53, 4.15 and  $\delta$  4.57, 4.01 are assigned to the ring protons of the major and minor isomers, respectively. Coupling constants of these protons for both diastereomers are in the range of 11 Hz, indicating  ${}^{3}J_{H-H}$  coupling. The C–C bond formation is thus believed to take place at the  $sp^3$  carbon of the azirinyl ring. This regiochemistry is different from that in the photolytically induced insertion reaction of ketone with organic azirine. The photoinduced addition of carbonyl groups of aldehydes, ketones, and esters to organic 2*H*-azirines is also completely regiospecific.<sup>27</sup> In the photoinduced addition reaction, the C-C bond formation takes place at the sp<sup>2</sup> carbon of the azirine ring. In our case the C-C bond formation at the  $sp^3$ carbon is confirmed by the single-crystal X-ray diffraction study described below. Usually, organic oxazolines are synthesized from nitrile or carboxylic acid derivates or amino alcohols, which could be easily prepared by the reduction of  $\alpha$ -amino acids, although other procedures are also used because of some particularly sensitive functionalities present on the precursors.<sup>28</sup>

The stereoselectivity of the insertion reaction is determined by the steric effect of substituents neighboring the carbonyl functionality. We carried out reactions of **3a** with a number of ketones and aldehydes. In the reaction of 3a with Me<sub>3</sub>CCHO only one diastereoisomer of 5d was isolated. The carbonyl group on the coordinated Cp ligand of CpFe(C<sub>5</sub>H<sub>4</sub>CHO) also inserts into the three-membered ring to give the single diastereoisomer 5e. Coupling constants between ring protons in the oxazolinyl groups in 5d,e are 9.3 and 9.4 Hz, respectively, indicating that the C-C bond formation takes place at the same carbon atom as that in 5c. Interestingly, the acetone moiety in the oxazolinyl ring of **5a** is irreversibly replaced by organic aldehyde. Namely, the reaction of **5a** with PhCHO yielded **5c**. Insertion of  $CO_2$ into the azirinyl ring has been reported, and  $CO_2$  can also be replaced by ketone, aldehyde, or other carbonylcontaining compounds.<sup>29</sup>

Treatment of **2b** with MeONa in acetone also affords the oxazolinyl complex **6a** in high yield. The coupling constant of 7.1 Hz between the internal vinyl proton and the ring proton is consistent with the formulation. For oxazolinyl complexes derived from **2c**, even though three

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	7a*	8a*	
mol formula	C54H67NOP2Ru	C49H54NO2P3F6Ru	
mol wt	909.10	996.91	
space group	Pbca	$P\overline{1}$	
a, Å	15.8700(3)	11.2850(2)	
b, Å	18.9940(3)	13.8970(2)	
<i>c</i> , Å	32.5140(8)	16.0390(3)	
α, deg	90.00	78.8460(10)	
$\beta$ , deg	90.00	83.4930(10)	
$\gamma$ , deg	90.00	75.9960(10)	
$V, Å^3$	9800.9(3)	2388.65(7)	
Z	8	2	
cryst dimens, mm <sup>3</sup>	0.25 imes 0.20 imes 0.20	$0.30\times0.25\times0.20$	
Mo Kα radiation, Å	0.710 73		
$\theta$ range, deg	1.79 - 25.00	2.13 - 25.00	
no. of rflns collected	38 008	$37\ 778$	
no. of indep rflns	8083	8418	
max, min transmissn	0.954, 0.795	0.959, 0.864	
no. of data/restraints/	8022/0/485	8401/2/558	
params			
GOF	2.130	1.332	
final R indices	R1 = 0.0711,	R1 = 0.0521,	
$(I > 2\sigma(I))$	wR2 = 0.1785	wR2 = 0.1529	
R indices	R1 = 0.1095,	R1 = 0.0631,	
(all data)	wR2 = 0.2140	wR2 = 0.1674	
$\Delta\delta$ (in final map), e/Å <sup>3</sup>	$-1.27, \pm 0.83$	-0.63, +1.23	

azirinyl intermediates are observed at the initial stage of the reaction of 2c with base in the absence of acetone, interestingly, the reaction of 2c with MeONa in acetone yields only the oxazolinyl complex 7a. We also prepared complexes 7b-e using similar procedures. For ketones and aldehydes, comparable stereoselectivity was observed for the formation of 7.

Insertion of a carbonyl group of an ester or an amide can also take place for **3c**. Thus, reactions of **3c** with methyl benzoate and with dimethylacetamide give **7f** in 77% yield and **7g** in 54% yield, respectively. The single Cp resonance in the NMR spectra of both **7f** and **7g** indicates high regio- and stereoselectivity in these reactions. In organic systems, no photoreaction has been reported between azirine and amide.

Treatment of complex  $2c^*$  with n-Bu<sub>4</sub>NOH in acetone affords  $7a^*$ , a product resulting from addition of acetone after deprotonation of  $2c^*$ , in 60% yield. In the <sup>1</sup>H NMR spectrum of  $7a^*$ , the <sup>1</sup>H singlet peak at  $\delta$  4.94 is assigned to CHPh of the oxazolinyl ring. Two inequivalent methyl groups of  $7a^*$  appear as two singlet resonances at  $\delta$  1.53 and 0.82. The characteristic  $C_{\alpha}$ resonance in the <sup>13</sup>C NMR spectrum of  $7a^*$  appears as a doublet of doublets at  $\delta$  193.7 with coupling constants of  $J_{P-C} = 18.8$  and 17.7 Hz. The <sup>31</sup>P NMR spectrum of  $7a^*$  displays two well-separated doublet resonances at  $\delta$  52.94 and 45.35 with  $J_{P-P} = 51.1$  Hz.

However, treatment of  $2c^*$  with NaOMe in the presence of KPF<sub>6</sub> in acetone solution affords [Ru\*]CNCHPhC(Me)<sub>2</sub>OH<sup>+</sup> (**8a**<sup>\*</sup>) in 38% yield. In the IR spectrum of **8a**<sup>\*</sup>, the absorption peak at 2118 cm<sup>-1</sup> is assigned to  $v_{C=N}$  stretching and the broad peak at 3576 cm<sup>-1</sup> is assigned to  $v_{OH}$ . In the <sup>1</sup>H NMR spectrum of **8a**<sup>\*</sup>, two <sup>1</sup>H singlet peaks at  $\delta$  5.46 and 2.53 are assigned to the CHPh and the OH absorptions, respectively, with the latter readily vanishing in the presence of D<sub>2</sub>O. The <sup>31</sup>P NMR spectrum of **8a**<sup>\*</sup> displaying AB type resonances at  $\delta$  38.44 and 38.06 with  $J_{P-P} = 46.5$  Hz differs significantly from that of **7a**<sup>\*</sup>.



Figure 2. ORTEP drawing of 7a\*.



Figure 3. ORTEP drawing of 8a\*.

Recrystallization of  $7a^*$  from *n*-hexane gives yellow crystals, and recrystallization of 8a\* from acetone/ diethyl ether (1:2) affords colorless crystals. The molecular structures of **7a**\* and **8a**\* have been confirmed by single-crystal X-ray diffraction studies (Table 1). ORTEP diagrams of **7a**\* and **8a**\* are shown in Figures 2 and 3, respectively, with selected bond distances and angles of **7a**<sup>\*</sup> and **8a**<sup>\*</sup> being listed in Tables 2 and 3, respectively. For  $7a^*$ , the C(1)-N(1) distance of 1.300(7) Å indicates a CN double bond.<sup>30</sup> The Ru(1)-C(1) distance of  $7a^*$  (2.054(5) Å) is slightly longer than the corresponding  $\operatorname{Ru}(1)-\operatorname{C}(1)$  distance of 8a\* (1.939(4) Å). In 8a\*, the Ru(1)-C(1) distance of 1.939(4) Å is typical of a Ru–C single bond. The C(1)–N(1) distance of 1.145(5) Å indicates a typical CN triple bond. The Ru(1)-C(1)-N(1) and  $C(1){-}N(1){-}C(2)$  angles are 172.2(3) and 173.0(4)°, respectively, indicating a linear isocyanide structure. The structure of the five-membered oxazolinyl ring confirms the regiospecific C-C bond formation. Previously, a bis(oxazoline) ligand was introduced as a chiral ligand for the preparation of asymmetric catalysts. These ligands use the nitrogen atom of the bis(oxazoline) to coordinate to the metal center rather

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 Table 2. Selected Bond Lengths (Å) and Bond

 Angles (deg) for Complex 7a\*

Bond Lengths						
Ru(1) - C(1)	2.054(5)	C(1) - O(1)	1.389(6)			
C(1) - N(1)	1.300(7)	O(1) - C(3)	1.464(6)			
N(1)-C(2)	1.464(7)	C(2) - C(3)	1.541(8)			
C(3) - C(4)	1.512(8)	C(3) - C(5)	1.512(8)			
C(2) - C(6)	1.512(8)	Ru(1) - P(1)	2.274(1)			
Ru(1) - P(2)	2.279(1)					
Bond Angles						
Ru(1) - C(1) - O(1)	115.0(3)	Ru(1) - C(1) - N(1)	133.2(4)			
C(1) - O(1) - C(3)	109.6(4)	C(1)-N(1)-C(2)	109.5(4)			
O(1) - C(3) - C(2)	100.5(4)	N(1)-C(2)-C(3)	104.5(4)			
O(1)-C(1)-N(1)	111.8(4)	O(1) - C(3) - C(4)	108.0(5)			
O(1) - C(3) - C(5)	107.7(5)	C(3) - C(2) - C(6)	115.9(4)			
N(1)-C(2)-C(6)	113.9(5)	P(1)-Ru(1)-P(2)	90.55(5)			

 Table 3. Selected Bond Lengths (Å) and Bond

 Angles (deg) for Complex 8a\*

Bond Lengths						
Ru(1) - C(1)	1.939(4)	C(1) - N(1)	1.145(5)			
N(1)-C(2)	1.458(5)	C(2) - C(3)	1.542(6)			
C(3) - O(1)	1.434(6)	C(3) - C(4)	1.510(8)			
C(3) - C(5)	1.525(7)	C(2) - C(6)	1.523(6)			
Ru(1) - P(1)	2.305(1)	Ru(1) - P(2)	2.309(1)			
Bond Angles						
Ru(1)-C(1)-N(1)	172.2(3)	C(1) - N(1) - C(2)	173.0(4)			
N(1)-C(2)-C(3)	107.9(3)	C(2) - C(3) - O(1)	102.6(4)			
C(2)-C(3)-C(4)	113.5(4)	C(2) - C(3) - C(5)	109.9(4)			
N(1)-C(2)-C(6)	110.5(3)	P(1)-Ru(1)-P(2)	90.91(3)			

than  $C_{\alpha}$  of the oxazolinyl ring in **7a**<sup>\*,31</sup> Treatment of **7a** with NaBH<sub>3</sub>CN in MeOH afforded the organic alcohol PhCH<sub>2</sub>CMe<sub>2</sub>OH and **1** in greater than 90% yield. Two products were separated by column chromatography. In the presence of D<sub>2</sub>O the reaction gave PhCH<sub>2</sub>-CMe<sub>2</sub>OD. NCC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CMe<sub>2</sub>OH and F<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>PhCH<sub>2</sub>-CMe<sub>2</sub>OH were also prepared from the corresponding complexes. The reaction in 0.1 g scale also occurred in hexane with slightly lower yield.<sup>32</sup>

**Concluding Remarks.** We prepared ruthenium azirinyl complexes by deprotonation reactions of ruthenium isocyanide complexes. In the ruthenium coordinated azirinyl system with a phenyl substituent three isomers, including a 1H-azirinyl complex, could be observed by NMR spectroscopy. Facile insertion of a carbonyl group of ketone, aldehyde, ester, and amide into the ruthenium-bound azirinyl ring to give oxazolinyl complexes followed a different regiospecificity from that in photolytic organic azirine systems. Subsequent hydride reduction releases organic alcohol and the ruthenium nitrile complex. Thus, C–C bond formation between organic halide and a carbonyl group could be catalyzed in a stepwise manner using the coordinated nitrile ligand.

#### **Experimental Section**

General Procedures. All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. CH<sub>2</sub>Cl<sub>2</sub> was distilled from CaH<sub>2</sub>, and diethyl ether and THF were distilled from Na/diphenylketyl. All other solvents and reagents were of reagent grade and were used as received. NMR spectra were recorded on Bruker AC-300 and DMX-500 FT-NMR spectrometers at room temperature (unless stated otherwise) and are reported in units of  $\delta$ with residual protons in the solvents as a reference (CDCl<sub>3</sub>,  $\delta$ 7.24:  $C_2D_6O$ ,  $\delta$  2.04). FAB mass spectra were recorded on a JEOL SX-102A spectrometer. Complexes [Ru]C≡N (1; [Ru] =  $(\eta^5 - C_5 H_5)(PPh_3)_2 Ru)$  and  $[Ru^*]C \equiv N$  (1\*;  $[Ru^*] = (\eta^5 - C_5 Me_5)$ -(dppp)Ru)<sup>33</sup> were prepared according to the methods reported in the literature. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument located at the National Taiwan University.

Preparation of {[Ru]CNCH<sub>2</sub>CN}Br (2a). To a sample of 1 (3.00 g, 4.18 mmol) dissolved in 70 mL of CHCl<sub>3</sub> at room temperature was added BrCH<sub>2</sub>CN (1.0 mL, 14.4 mmol) via a syringe. The resulting mixture was heated to reflux for 2 days. After removal of all volatile substances in vacuo, 10 mL of CH<sub>2</sub>Cl<sub>2</sub> was added to the residue under nitrogen, and the mixture was added to a vigorously stirred ether solution (100 mL) to cause green solid to precipitate out. The solid product was collected by filtration followed by washing with ether and was identified as 2a (2.63 g, 75% yield). Spectroscopic data for 2a: <sup>1</sup>H NMR (CDCl<sub>3</sub>) & 7.32-7.05 (m, 30H, Ph), 5.51 (s, 2H, CH<sub>2</sub>), 4.86 (s, 5H, Cp); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  165.1 (t,  $J_{C-P}$  $= 19.9 \text{ Hz}, C_{\alpha}$ , 135.3–127.5 (Ph), 111.8 (CN), 88.4 (Cp), 35.4 (CH<sub>2</sub>); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  45.4; MS (FAB, *m/z*, Ru<sup>102</sup>) 757 (M<sup>+</sup>), 495 ( $M^+$  – PPh<sub>3</sub>). Anal. Calcd for  $C_{44}H_{37}N_2P_2BrRu: C, 63.16;$ H, 4.46; N, 3.35. Found: C, 63.31; H, 4.59; N, 3.40.

Other isocyanide complexes  $\{[Ru]CNCH_2R\}X$  (R = CH=  $CH_2$ , **2b**, 90% yield;  $R = C_6H_5$ , **2c**, 92% yield;  $R = COOCH_3$ , 2d, 74% yield) were prepared similarly from the reactions of 1 with ICH<sub>2</sub>CH=CH<sub>2</sub>, BrCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, and BrCH<sub>2</sub>COOCH<sub>3</sub>, respectively. Spectroscopic data for 2b: <sup>1</sup>H NMR (CDCl<sub>3</sub>) & 7.36-7.04 (m, 30H, Ph), 5.59 (ddt,  $J_{\rm H-H}$  = 15.4, 10.0, 7.2 Hz, 1H, =CH), 5.16 (d,  $J_{\rm H-H}$  = 15.4 Hz, 1H, =CH), 5.09 (d,  $J_{\rm H-H}$  = 10.0 Hz, 1H, =CH), 4.79 (s, 5H, Cp), 4.57 (d,  $J_{\rm H-H}$  = 7.2 Hz, CH<sub>2</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  153.0 (t,  $J_{C-P} = 21.0$  Hz,  $C_{\alpha}$ ), 135.8– 128.3 (Ph), 129.3 (CH), 118.9 (CH<sub>2</sub>), 87.6 (Cp), 49.2 (CH<sub>2</sub>); <sup>31</sup>P NMR (CDCl<sub>3</sub>) & 46.3; MS (FAB, m/z, Ru<sup>102</sup>) 758 (M<sup>+</sup>), 496 (M<sup>+</sup> - PPh<sub>3</sub>), 429 (M<sup>+</sup> - PPh<sub>3</sub>-CNC<sub>3</sub>H<sub>5</sub>). Anal. Calcd for C<sub>45</sub>H<sub>40</sub>-NP<sub>2</sub>IRu: C, 61.09; H, 4.56; N, 1.58. Found: C, 61.15; H, 4.64; N, 1.49. Spectroscopic data for 2c: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.34 6.92 (m, 30H, Ph), 5.11 (s, 2H, CH<sub>2</sub>), 4.77 (s, 5H, Cp); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  45.4; MS (FAB, m/z, Ru<sup>102</sup>) 808 (M<sup>+</sup>), 546 (M<sup>+</sup>) PPh<sub>3</sub>). Anal. Calcd for C<sub>49</sub>H<sub>42</sub>NP<sub>2</sub>BrRu: C, 66.29; H, 4.77; N, 1.58. Found: C, 66.25; H, 4.83; N, 1.62. Spectroscopic data for 2d: <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.28-7.05 (m, 30H, Ph), 4.92 (s, 2H, CH\_2), 4.76 (s, 5H, Cp), 3.60 (s, 3H, CH\_3);  $^{13}\mathrm{C}$  NMR (CDCl\_3)  $\delta$ 165.4 (C=O), 158.2 (t,  $J_{C-P} = 20.2 \text{ Hz}, C_{\alpha}$ ), 135.5–127.6 (Ph), 87.7 (Cp), 52.5 (CH<sub>2</sub>), 47.8 (CH<sub>3</sub>); <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 46.0; MS  $(FAB, m/z, Ru^{102})$  790  $(M^+)$ , 528  $(M^+ - PPh_3)$ . Anal. Calcd for C<sub>45</sub>H<sub>40</sub>NO<sub>2</sub>P<sub>2</sub>BrRu: C, 62.14; H, 4.64; N, 1.61. Found: C, 62.39; H, 4.89; N, 1.70.

Synthesis of {[Ru\*]CNCH<sub>2</sub>Ph}Br (2c\*). To a Schlenk flask charged with [Ru\*]CN (1\*; 0.20 g, 0.30 mmol) and CHCl<sub>3</sub> (40 mL) was added BrCH<sub>2</sub>Ph (0.20 mL, 1.16 mmol). The clear solution was heated to reflux for 6 h. After the mixture was cooled, the solvent was reduced to about 5 mL. The mixture was slowly added to a diethyl ether solution (90 mL). The white precipitate thus formed was filtered off and washed with diethyl ether and *n*-hexane. The product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane (1:10) and was identified as **2c**\* (0.14

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g, 57% yield). Spectroscopic data for  $2c^*$ : IR (KBr) 2115 cm $^{-1}$  (s,  $\nu_{\rm CN}$ ); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.42–7.08 (m, 30H, Ph), 5.18 (s, 2H, CH<sub>2</sub>), 2.59–1.52 (m, 6H, CH<sub>2</sub>), 1.34 (s, 15H, 5 CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  160.6 (t,  $J_{\rm P-C}$  = 19.4 Hz, CN), 136.1–128.1 (Ph), 96.6 (s, Cp), 50.1 (s, CH<sub>2</sub>), 30.4 (t,  $J_{\rm P-C}$  = 17.5 Hz, CH<sub>2</sub>), 20.9 (s, CH<sub>2</sub>), 9.7 (s, 5CH<sub>3</sub>)' <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  37.80; MS (FAB, m/z, Ru<sup>102</sup>) 766.3 (M<sup>+</sup>), 649.3 (M<sup>+</sup> – CNCH<sub>2</sub>Ph). Anal. Calcd for C45H48NP<sub>2</sub>RuBr: C, 63.90; H, 5.68; N, 1.66. Found: C, 64.11; H, 5.99; N, 1.32.

Synthesis of 3a. To a solution of 2a (0.12 g, 0.14 mmol) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> at 0 °C was added a solution of *n*-Bu<sub>4</sub>NOH (0.5 mL, 1 M in MeOH). The mixture was stirred for 10 min, and the color changed from green to yellow. Then the solvent was removed under vacuum at 0 °C and the solid residue was extracted with cool ether. The extract was filtered through Celite. Solvent of the filtrate was removed under vacuum to give **3a** (0.10 g, 94% yield). Complex **3a** is thermally unstable and decomposes to some unidentifiable products in solution over 30 min. Spectroscopic data for 3a: <sup>1</sup>H NMR (CD<sub>3</sub>CN, -20 °C) & 7.63-7.18 (m, 30H, Ph), 4.26 (s, 5H, Cp), 2.98 (s, 1H, CH); <sup>13</sup>C NMR (CD<sub>3</sub>CN, -20 °C)  $\delta$  184.3 (t,  $J_{P-C} = 19.9$  Hz, C<sub>α</sub>), 138.1–127.3 (Ph), 119.3 (CN), 88.9 (Cp), 11.3 (CH); <sup>31</sup>P NMR (CD<sub>3</sub>CN, -20 °C)  $\delta$  49.1, 48.7 (2d,  $J_{P-P} = 34.8$  Hz). MS (FAB) m/z: 757.3 (M<sup>+</sup> + 1), 495.0 (M<sup>+</sup> + 1 - PPh<sub>3</sub>), 429.0 (M<sup>+</sup> + 1 - PPh<sub>3</sub>, CNCHCN). The elemental analysis is not satisfactory, possibly due to the instability of 3a.

Synthesis of 3b. To a solution of 2b (0.10 g, 0.13 mmol) in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> at 0 °C was added a THF solution of *n*-Bu<sub>4</sub>NF. The mixture was stirred for 10 min, and the color changed to bright yellow. Then the solvent was removed under vacuum at 0 °C and the solid residue was extracted with cool hexane. The extract was filtered through Celite. The solvent of the filtrate was removed under vacuum to give **3b** (0.087 g, 88% yield). Complex **3b** is soluble in THF, ether, and hexane and is thermally unstable, decomposing to some unidentifiable products. Spectroscopic data for **3b**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 10 °C)  $\delta$  $7.42-7.06 \text{ (m, 30H, PPh_3)}, 5.73 \text{ (ddd, } J_{H-H} = 18.2, 9.1, 7.2 \text{ Hz},$ 1H, =CH), 5.26 (d,  $J_{H-H}$  = 18.2 Hz, 1H, =CH), 5.21 (d,  $J_{H-H}$ = 9.1 Hz, 1H, =CH), 4.73 (s, 5H, Cp), 2.76 (d,  $J_{H-H}$  = 7.2 Hz, 1H, CNCH); <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>, 10 °C)  $\delta$  52.0, 48.8 (AB,  $J_{P-P} =$ 34.8 Hz); MS (FAB, m/z) 758.2 (M<sup>+</sup> + 1), 496.1, (M<sup>+</sup> + 1 - $PPh_3$ ), 429,0 (M<sup>+</sup> + 1 - PPh<sub>3</sub>, CNCH=CH<sub>2</sub>).

Reaction of {[Ru]CNCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>}Br with n-Bu<sub>4</sub>NOH. To a solution of 2c (0.14 g, 0.16 mmol) in 20 mL of acetone was added a solution of *n*-Bu<sub>4</sub>NOH (0.5 mL) at 0 °C. The mixture was stirred for 10 min, and the color changed to yellow-orange. Then the solvent was removed under vacuum and the solid residue was extracted with ether at 0 °C. The extract was filtered through Celite. The solvent of the filtrate was removed under vacuum at 0 °C to give the products 3c (0.12 g, 95%) yield). Three isomers are observed in the spectra of 3c at -20°C. Spectroscopic data for **3c**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> at -20 °C) δ 7.55-6.94 (m, Ph), 4.89, 4.71 (2s, 1H, CH), 4.59, 4.58, 4.57 (3s, 5H, Cp), 3.23 (br, 1H, NH); <sup>31</sup>P NMR (C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> at -20 °C)  $\delta$  51.98, 48.82 (2d,  $J_{\rm P-P}=$  34.8 Hz), 51.89, 49.72 (2d,  $J_{\rm P-P}$ = 34.8 Hz), 51.17, 50.15 (2d,  $J_{P-P}$  = 34.9 Hz); MS (FAB of the mixture, m/z) 808.4 (M<sup>+</sup> + 1), 546.2 (M<sup>+</sup> + 1 - PPh<sub>3</sub>), 429.0  $(M^+ + 1 - PPh_3, CNCH_2Ph)$ ; high-resolution MS (FAB, m/z) calcd for  $C_{49}H_{42}RuP_2N$  (M + 1) 808.1850, found 808.1836. Complex 3c in pure form was not obtained. Variable-temperature NMR data were collected in  $C_6D_5CD_3$ , and at -40 °C only one isomer is observed.

**Reaction of 2d with** *n***-Bu**<sub>4</sub>**NOH.** To a solution of **2d** (0.14 g, 0.16 mmol) in 20 mL of acetone was added a solution of *n*-Bu<sub>4</sub>NOH (0.5 mL). The mixture was stirred for 10 min, and the color changed to orange. Then the solvent was removed under vacuum and the solid residue was extracted with ether. The extract was filtered through Celite. The solvent of the filtrate was removed under vacuum to give **4d** (0.090 g, 72% yield) after recrystallization from ether. Spectroscopic data for **4d**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.65–7.00 (m, 30H, Ph), 4.69 (s, 5H,

Cp), 4.13 (s, 2H, CH<sub>2</sub>); <sup>31</sup>P NMR (CD<sub>3</sub>COCD<sub>3</sub>)  $\delta$  50.5; MS (FAB, m/z) 776.2 (M<sup>+</sup> + 1), 514.0 (M<sup>+</sup> + 1 - PPh<sub>3</sub>), 428.9 (M<sup>+</sup> + 1 - PPh<sub>3</sub>, CNCH<sub>2</sub>CO<sub>2</sub>).

Synthesis of 5a. To a solution of 2a (0.11 g, 0.13 mmol) in 10 mL of acetone was added a solution of *n*-Bu<sub>4</sub>NOH (0.20 mL). The color of the solution changed from green to yellow immediately. The solvent was removed under vacuum, the residue was extracted with hexane, and then after filtration the solution was dried under vacuum to afford the yellow product **5a** (0.080 g, 82% yield). Spectroscopic data of **5a**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) & 7.44-6.99 (m, 30 H, Ph), 4.48 (s, 5H, Cp), 4.03 (s, 1H, CH), 1.32 (s, 3H, Me), 0.82 (s, 3H, Me); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  197.6 (t,  $J_{P-C} = 18.8$  Hz,  $C_{\alpha}$ ), 140.4–127.4 (Ph), 119.2 (CN), 86.3 (Cp), 79.5 (C(Me)<sub>2</sub>), 68.2 (CH), 27.8 (CH<sub>3</sub>), 25.3 (CH<sub>3</sub>); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  51.0, 50.0 (AB,  $J_{P-P} = 34.5$  Hz); MS (FAB, m/z) 815.3 (M<sup>+</sup> + 1), 553.1 (M<sup>+</sup> + 1 - PPh<sub>3</sub>), 429.0 (M<sup>+</sup> + 1 - PPh<sub>3</sub>)  $PPh_3 - CNCHCNC(CH_3)_2O$ ). Anal. Calcd for  $C_{47}H_{42}N_2OP_2Ru$ : C, 69.36; H, 5.20; N, 3.44. Found: C, 69.47; H, 5.44; N, 3.27. Complex **5a** can also be obtained from the reaction of **3a** with acetone.

Complex 5b (79% yield) was similarly prepared from 2a (0.076 g) and 2-butanone (0.012 mL, 0.10 mmol) and *n*-Bu<sub>4</sub>NOH (0.5 mL) in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> at room temperature. A mixture containing two diastereomers (5:4) was isolated. Spectroscopic data for **5b**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, major product)  $\delta$  7.62–7.00 (m, 30 H,  $PPh_3),\,4.51$  (s, 5H, Cp), 4.22 (s, 1H, CH), 1.78 (m, 1H,  $CH_2),\ 1.58$  (m, 1H,  $CH_2),\ 1.27$  (s, 3H, Me), 0.88 (m, 3H, CH<sub>2</sub>CH<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>, minor product)  $\delta$  7.62–7.00 (m, 30 H, PPh<sub>3</sub>), 4.53 (s, 5H, Cp), 4.19 (s, 1H, CH), 1.78 (m, 1H, one proton of  $CH_2$ ), 1.58 (m, 1H, one proton of  $CH_2$ ), 0.97 (t,  $J_{\rm H-H} = 7.1$  Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 0.79 (s, 3H, Me); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, major product)  $\delta$  197.4 (t,  $J_{P-C} = 19.3$  Hz,  $C_{\alpha}$ ), 140.6–123.9 (Ph), 118.4 (CN), 82.8 (Cp), 75.5 (CMeEt), 69.1 (CH), 29.8 (CH<sub>2</sub>), 24.1 (CH<sub>3</sub>), 8.5 (CH<sub>3</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, minor product)  $\delta$  197.9 (t,  $J_{P-C} = 19.6$  Hz,  $C_{\alpha}$ ), 140.6–123.9 (Ph), 117.9 (CN), 82.6 (Cp), 75.1 (CMeEt), 70.2 (CH), 26.8 (CH<sub>2</sub>), 23.8 (CH<sub>3</sub>), 9.1 $(CH_3)$ ; <sup>31</sup>P NMR  $(C_6D_6) \delta$  52.6, 49.7  $(AB, J_{P-P} = 34.1 \text{ Hz})$ , 52.3, 49.7 (AB,  $J_{P-P} = 34.3$  Hz) (5:4); MS (FAB, m/z) 829.2 (M<sup>+</sup> + 1), 567.3 (M<sup>+</sup> + 1 - PPh<sub>3</sub>), 429.0 (M<sup>+</sup> - PPh<sub>3</sub>, CNCHCNC-(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>3</sub>)O). Anal. Calcd for C<sub>48</sub>H<sub>44</sub>N<sub>2</sub>OP<sub>2</sub>Ru: C, 69.63; H, 4.91; N, 3.25. Found: C, 69.38; H, 4.97; N, 3.09.

Complex 5c (87% yield) was similarly prepared from 2a (0.051 g, 0.061 mmol), benzaldehyde (0.0062 mL, 0.061 mmol), and n-Bu<sub>4</sub>NOH (0.5 mL) in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> at room temperature. A mixture containing two diastereomers in a 5:1 ratio was isolated. Spectroscopic data for 5c: 1H NMR (CDCl<sub>3</sub>, major isomer)  $\delta$  7.62–6.80 (m, 35 H, Ph), 4.53 (d, 1H,  $J_{\text{H-H}} = 11.4$ Hz, CH), 4.51 (s, 5H, Cp), 4.15 (d, 1H,  $J_{H-H} = 11.4$  Hz, CH); <sup>1</sup>H NMR (CDCl<sub>3</sub>, minor isomer)  $\delta$  7.62–6.80 (m, 35 H, Ph), 4.57 (d, 1H,  $J_{H-H} = 11.4$  Hz, OCH), 4.41 (s, 5H, Cp), 4.01 (d, 1H,  $J_{\text{H-H}} = 11.4$  Hz, CCH); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, major isomer)  $\delta$ 197.5 (t,  $J_{P-C} = 19.7$  Hz,  $C_{\alpha}$ ), 139.1–121.6 (Ph), 119.5 (CN), 86.4 (CHPh), 85.6 (Cp), 80.1 (CH); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, minor isomer)  $\delta$  196.4 (t,  $J_{P-C} = 19.6$  Hz,  $C_{\alpha}$ ), 119.1 (CN), 85.3 (CHPh), 85.1 (Cp), 78.3 (CH); <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>) & 51.8, 49.4 (AB,  $J_{P-P} = 34.5$  Hz), 51.2, 49.7 (AB,  $J_{P-P} = 34.4$  Hz) (5:1); MS (FAB, m/z) 863.1  $(M^+ + 1)$ , 602.3  $(M^+ + 1 - PPh_3)$ , 429.0  $(M^+$ PPh<sub>3</sub>, CNCHCNCPhHO). Anal. Calcd for C<sub>51</sub>H<sub>42</sub>N<sub>2</sub>OP<sub>2</sub>Ru: C, 71.07; H, 4.91; N, 3.25. Found: C, 71.35; H, 4.69; N, 3.58.

Complex **5d** was prepared using the following method. A mixture of complex **3a** (0.22 g, 0.30 mmol) and trimethylacetaldehyde (0.03 mL, 0.3 mmol) in 10 mL of benzene was heated to reflux for 1 h. The workup procedure was the same as that for **5a**. Only one isomer is observed. Purification by recrystallization of the product from CH<sub>2</sub>Cl<sub>2</sub>/ether (1:3) gave **5d** (0.19 g, 78% yield). Spectroscopic data for **5d**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.62–6.94 (m, 30 H, PPh<sub>3</sub>), 4.48 (s, 5H, Cp), 4.05 (d, 1H, J<sub>H-H</sub> = 9.3 Hz, CHCN), 3.80 (d, 1H, J<sub>H-H</sub> = 9.3 Hz, OCH), 0.94 (s, 9H, C(CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  195.1 (t, J<sub>P-C</sub> = 19.4 Hz, C<sub>a</sub>), 139.4–122.8 (Ph), 118.1 (CN), 81.7 (Cp), 76.4 (CC(CH<sub>3</sub>)<sub>3</sub>), 70.3 (CH), 57.1 (CMe<sub>3</sub>), 29.4 (CMe<sub>3</sub>); <sup>31</sup>P NMR  $\begin{array}{l} ({\rm C}_6{\rm D}_6) \ \delta \ 51.6, \ 49.6 \ ({\rm AB}, \ J_{\rm P-P} = 34.2 \ {\rm Hz}); \ {\rm MS} \ ({\rm FAB}, \ m/z) \ 843.3 \\ ({\rm M}^+ \ + \ 1), \ 581.1 \ ({\rm M}^+ \ + \ 1 \ - \ {\rm PPh}_3), \ 429.0 \ ({\rm M}^+ \ - \ {\rm PPh}_3), \\ {\rm CNCHCNCHCMe_3O).} \ {\rm Anal.} \ {\rm Calcd} \ {\rm for} \ {\rm C}_{49}{\rm H}_{46}{\rm N}_2{\rm OP}_2{\rm Ru}: \ {\rm C}, \\ {\rm 69.90}; \ {\rm H}, \ 5.51; \ {\rm N}, \ 3.33. \ {\rm Found:} \ {\rm C}, \ 70.00; \ {\rm H}, \ 5.58; \ {\rm N}, \ 3.39. \end{array}$ 

Synthesis of 5e. To 50 mL of a CH<sub>2</sub>Cl<sub>2</sub> solution of 2a (0.07 g, 0.084 mmol) were added a slight excess of ferrocenecarboxaldehyde (0.02 g, 0.12 mmol) and n-Bu<sub>4</sub>NOH (0.5 mL), and the solution was heated to reflux for 90 min. The color changed from yellow to bright yellow, and then the solvent was removed under vacuum. The residual solid was extracted with  $2 \times 20$ mL of ether, and the solution was filtered through Celite. The solvent of the filtrate was removed under vacuum to give 5e (0.054 g, 67% yield). Spectroscopic data for 5e: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.56–7.01 (m, 30 H, Ph), 5.09 (d, 1H,  $J_{\text{H-H}}$  = 9.4 Hz, OCH), 4.47 (s, 5H, Cp), 4.21 (d, 1H,  $J_{\rm H-H} = 9.4$  Hz, NCH), 4.07 (br, 2H, Fe(C<sub>5</sub>H<sub>4</sub>)CO), 4.05 (br, 2H, Fe(C<sub>5</sub>H<sub>4</sub>)CO), 3.94 (s, 5H,  $(C_5H_5)Fe)$ ; <sup>13</sup>C NMR  $(C_6D_6) \delta$  197.5 (t,  $J_{P-C} = 19.7$  Hz,  $C_{\alpha}$ ), 139.1-121.6 (m, Ph), 119.5 (CN), 99.1 (CHFe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>), 85.6 (Cp), 80.7 (CHCN), 71.4 (C<sub>5</sub>H<sub>5</sub>), 68.6 (C<sub>5</sub>H<sub>5</sub>), 64.6 (C<sub>5</sub>H<sub>5</sub>), 64.1  $(C_5H_5)$ ; <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  51.3, 50.8 (AB,  $J_{P-P} = 34.9$  Hz); MS (FAB, m/z) 971.3 (M<sup>+</sup> + 1), 709.2 (M<sup>+</sup> + 1 - PPh<sub>3</sub>), 429.0  $(M^+ - PPh_3, CNCHCNCH Fe(C_5H_5)_2O)$ . Anal. Calcd for C<sub>55</sub>H<sub>46</sub>N<sub>2</sub>OP<sub>2</sub>RuFe: C, 68.11; H, 4.78; N, 2.89. Found: C, 68.15; H, 4.80; N, 3.01.

Synthesis of 6a. To a solution of 2b (0.11 g, 0.13 mmol) in 20 mL of acetone was added a solution of *n*-Bu<sub>4</sub>NOH (0.5 mL). The color of the solution changed from yellow to bright yellow immediately. The solvent was removed under vacuum, the residue was extracted with hexane, and then the solution was dried under vacuum to afford 6a (0.092 g, 91% yield). Spectroscopic data of  $\mathbf{6a:}~^1\mathrm{H}$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.55–6.97 (m, 30 H,  $PPh_3$ ), 5.69 (ddd,  $J_{H-H} = 16.9, 9.9, 7.1 Hz, 1H, HC =$ ), 5.23 (dd,  $J_{\rm H-H} = 16.9, 2.4 \, \text{Hz}, 1\text{H}, = \text{CH}H), 5.01 \, (\text{dd}, J_{\rm H-H} = 9.9, 2.4 \, \text{Hz},$ 1H, =CHH), 4.57 (s, 5H, Cp), 4.01 (d, 1H,  $J_{H-H}$  = 7.1 Hz), 1.15 (s, 3H, Me), 1.05 (s, 3H, Me);  $^{13}$ C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  198.4 (t,  $J_{P-C}$ = 18.1 Hz,  $C_{\alpha}$ ), 152.4 (CH=CH<sub>2</sub>), 142.3-123.6 (Ph), 110.4 (CH=CH<sub>2</sub>), 83.7 (Cp), 78.4. (CMe<sub>2</sub>), 64.1 (CH), 28.5 (CH<sub>3</sub>), 24.2 (CH<sub>3</sub>); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  51.2, 50.4 (AB,  $J_{P-P} = 34.7$  Hz); MS (FAB, m/z) 816.3 (M<sup>+</sup> + 1), 554.1 (M<sup>+</sup> + 1 - PPh<sub>3</sub>), 429.0 (M<sup>+</sup> - PPh<sub>3</sub>, CNCH(HC=CH<sub>2</sub>)C(CH<sub>3</sub>)<sub>2</sub>O). Anal. Calcd for C<sub>48</sub>H<sub>45</sub>NOP<sub>2</sub>Ru: C, 70.75; H, 5.57; N, 1.72. Found: C, 70.86; H, 5.49; N, 1.99.

Synthesis of 7a. To a solution of 2c (0.086 g, 0.10 mmol) in 20 mL of acetone at room temperature was added a solution of n-Bu<sub>4</sub>NOH (0.1 mL). The mixture was stirred for 5 min, and the color changed from green to yellow. Then the solvent was removed under vacuum and the solid residue was extracted with hexane. The extract was filtered through Celite. The solvent of the filtrate was removed under vacuum to give 7a~(0.08~g,~91% yield). Spectroscopic data for  $7a:~^1H$  NMR (C<sub>6</sub>D<sub>6</sub>) & 7.79-7.15 (m, 35 H, Ph), 4.93 (s, 1H, CH), 4.80 (s, 5H, Cp), 1.52 (s, 3H, Me), 0.98 (s, 3H, Me);  $^{13}$ C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  $187.3 (t, J_{P-C} = 19.4 \text{ Hz}, C_{\alpha}), 143.6 - 126.9 (Ph), 87.5 (Cp), 85.9$ (CH), 79.8 (CMe<sub>2</sub>), 28.3 (CH<sub>3</sub>), 27.9 (CH<sub>3</sub>); <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>) δ 51.8, 50.1 (AB,  $J_{P-P} = 34.6$  Hz); MS (FAB) m/z: 866.3 (M<sup>+</sup> + 1), 604.1 ( $M^+$  + 1 - PPh<sub>3</sub>), 429.0 ( $M^+$  + 1 - PPh<sub>3</sub>, CNCHPhC-Me<sub>2</sub>O). Anal. Calcd for C<sub>52</sub>H<sub>47</sub>NOP<sub>2</sub>Ru: C, 72.41; H, 5.38; N, 1.60. Found: C, 72.19; H, 5.53; N, 1.69.

Synthesis of 7a<sup>\*</sup>. To a solution of 2c<sup>\*</sup> (0.25 g, 0.30 mmol) in 20 mL of acetone was added a solution of n-Bu<sub>4</sub>NOH (0.31 mL). The color of the solution changed to yellow immediately. The mixture was stirred for 10 min. The solvent was removed under vacuum, the residue was extracted with *n*-hexane, and then the solution was dried under vacuum to afford 7a<sup>\*</sup>. Complex 7a<sup>\*</sup> was recrystallized from *n*-hexane (0.15 g, 60% yield). Spectroscopic data for 7a<sup>\*</sup>: IR (KBr) 1633 cm<sup>-1</sup> (m,  $\nu_{C=N}$ ); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.78–6.72 (m, 25H, Ph), 4.94 (s, 1H, CHPh), 4.12–4.05 (m, 1H, dppp), 3.55–3.46 (m, 1H, dppp), 2.34–2.27 (m, 1H, dppp), 1.92–1.66 (m, 3H, dppp), 1.53 (s, 3H, CH<sub>3</sub>), 1.50 (s, 15H, 5CH<sub>3</sub>), 0.82 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  193.7 (dd,  $J_{P-C} = 18.8$  Hz,  $J_{P-C} = 17.7$  Hz), 145.8–

125.9, (Ph), 94.3 (s, Cp), 80.8 (s, CHPh), 29.3 (dppp), 29.2 (s, CMe<sub>2</sub>), 25.2 (s, Me<sub>2</sub>), 24.8 (m, dppp), 10.5 (s, 5Me); <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  52.94, 45.35 (2 d,  $J_{P-P} = 51.1$  Hz); MS (FAB, m/z, Ru<sup>102</sup>): 824.2 (M<sup>+</sup>), 766.2 (M<sup>+</sup> – CO(CH<sub>3</sub>)<sub>2</sub>). Anal. Calcd for C<sub>48</sub>H<sub>53</sub>NOP<sub>2</sub>Ru: C, 70.07; H, 6.45; N, 1.70. Found: C, 70.32; H, 6.43; N, 1.69.

**Synthesis of 7b.** Complex **7b** (87% yield) was similarly prepared from **3c** (0.051 g) and benzaldehyde in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> at room temperature. Spectroscopic data for **7b**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, major isomer)  $\delta$  7.58–6.94 (m, 40 H, Ph), 5.12 (d, 1H, J<sub>H-H</sub> = 11.4 Hz, NCHPh), 4.64 (s, 5H, Cp), 4.49 (d, 1H, J<sub>H-H</sub> = 11.4 Hz, OCHPh); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, minor isomer)  $\delta$  7.58–6.94 (m, 40 H, Ph), 5.12 (d, 1H, J<sub>H-H</sub> = 11.4 Hz, OCHPh); <sup>3</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, minor isomer)  $\delta$  7.58–6.94 (m, 40 H, Ph), 5.12 (d, 1H, J<sub>H-H</sub> = 11.4 Hz, OCHPh), 4.73 (s, 5H, Cp), 4.49 (d, 1H, J<sub>H-H</sub> = 11.4 Hz, NCHPh); <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  51.8, 49.3 (AB, J<sub>P-P</sub> = 34.7 Hz), 51.0, 49.7 (AB, J<sub>P-P</sub> = 34.6 Hz) (4:1); MS (FAB, *m/z*) 914.2 (M<sup>+</sup> + 1), 651.2 (M<sup>+</sup> + 1 - PPh<sub>3</sub>), 429.0 (M<sup>+</sup> - PPh<sub>3</sub>, CNCHPhCPhHO). Anal. Calcd for C<sub>56</sub>H<sub>47</sub>NOP<sub>2</sub>Ru: C, 73.67; H, 5.19; N, 1.53. Found: C, 73.49; H, 5.33; N, 1.50.

**Synthesis of 7c.** Complex **7c** (81% yield) was similarly prepared from **3c** (0.096 g) and 2-butanone (0.010 mL, 0.12 mmol) in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> at room temperature. Spectroscopic data for **7c**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, major)  $\delta$  7.57–6.99 (m, 35H, Ph), 4.85 (s, 1H, CH), 4.63 (s, 5H, Cp), 1.78 (m, 1H, CH<sub>2</sub>), 1.58 (m, 1H, CH<sub>2</sub>), 1.24 (s, 3H, Me), 0.87 (m, 3H, CH<sub>3</sub>); <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, minor)  $\delta$  7.57–6.99 (m, 35 H, Ph), 4.76 (s, 1H, CH), 4.61 (s, 5H, Cp), 1.78 (m, 1H, CH<sub>2</sub>), 0.96 (t, J<sub>H-H</sub> = 7.3 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 0.64 (s, 3H, Me); <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  52.1, 49.6 (AB, J<sub>P-P</sub> = 34.7 Hz), 52.2, 49.6 (AB, J<sub>P-P</sub> = 34.6 Hz) (5: 4); MS (FAB, *m*/*z*) 880.3 (M<sup>+</sup> + 1), 618.2 (M<sup>+</sup> + 1 - PPh<sub>3</sub>), 429.0 (M<sup>+</sup> - PPh<sub>3</sub>, CNCHPhCMe(Et)O). Anal. Calcd for C<sub>53</sub>H<sub>49</sub>-NOP<sub>2</sub>Ru: C, 72.42; H, 5.62; N, 1.59. Found: C, 72.49; H, 5.57; N, 1.63.

Synthesis of 7d. Complex 7d was prepared using the following method. A mixture of complex 3c (0.48 g) and trimethylacetaldehyde (0.1 mL, 0.1 mmol) in 40 mL of benzene was heated to reflux for 1 h. The workup procedure was the same as that for 7d. Purification by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:5) gave 7d (0.46 g, 87% yield). Spectroscopic data for 7d: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.64–6.97 (m, 35 H, Ph), 4.96 (d, 1H,  $J_{H-H} = 9.7$  Hz, NCHPh), 4.67 (s, 5H, Cp), 3.82 (d, 1H,  $J_{H-H} = 9.7$  Hz, OCH); <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  52.0, 48.9 (AB,  $J_{P-P} = 34.7$  Hz); MS (FAB, m/z) 894.3 (M<sup>+</sup> + 1), 632.2 (M<sup>+</sup> + 1 – PPh<sub>3</sub>), 429.0 (M<sup>+</sup> – PPh<sub>3</sub>, CNCHPhCHC(Me)<sub>3</sub>O). Anal. Calcd for C<sub>54</sub>H<sub>51</sub>NOP<sub>2</sub>Ru: C, 72.63; H, 5.76; N, 1.57. Found: C, 72.90; H, 5.51; N, 1.38.

Synthesis of 7e. To a 50 mL  $CH_2Cl_2$  solution of 2c (0.47 g, 0.53 mmol) were added excess ferrocenecarboxaldehyde (0.14 g, 0.67 mmol) and n-Bu<sub>4</sub>NOH (0.7 mL), and the solution was heated to reflux for 90 min. The color changed from yellow to bright yellow, and then the solvent was removed under vacuum. The residual solid was extracted with  $2 \times 20$  mL of hexane, and the solvent was filtered through Celite. The solvent of the filtrate was removed under vacuum to give 7e (0.45 g, 83% yield). Spectroscopic data for 7e:  $^{1}H$  NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.52–6.98 (m, 35 H, Ph), 5.06 (d, 1H,  $J_{\rm H-H}$  = 9.5 Hz, NCHPh), 4.64 (s, 5H, Cp), 4.53 (d, 1H,  $J_{H-H} = 9.5$  Hz, OCH), 4.04 (br, 2H, Fe(C<sub>5</sub>H<sub>4</sub>)CO), 3.97 (br, 2H, Fe(C<sub>5</sub>H<sub>4</sub>)CO), 3.91 (s, 5H, (C<sub>5</sub>H<sub>5</sub>)Fe); <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  51.0, 50.7 (AB,  $J_{P-P} = 35.1$ Hz); MS (FAB, m/z) 1021.1 (M<sup>+</sup> + 1), 759.2 (M<sup>+</sup> + 1 - PPh<sub>3</sub>), 429.0 ( $M^+$  – PPh<sub>3</sub>), CNCHPhCH, Fe( $C_5H_5$ )<sub>2</sub>O). Anal. Calcd for C<sub>60</sub>H<sub>51</sub>NOP<sub>2</sub>RuFe: C, 70.59; H, 5.04; N, 1.37. Found: C, 70.72; H, 4.97; N, 1.54.

Synthesis of 7f. A mixture of complex 3c (0.27 g, 0.33 mmol) and methyl benzoate (0.062 mL, 0.5 mmol) in 40 mL of benzene was heated to reflux for 3 h. The workup procedure was the same as that for 7a. Purification by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:5) gave 7f (0.23 g, 77% yield). Spectroscopic data for 7f: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.33–6.08 (m, 40 H, Ph), 5.02 (s, 1H, CH), 4.83 (s, 5H, Cp), 3.66 (s, 3H, Me); <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  52.3, 48.9 (AB,  $J_{P-P} = 34.4$  Hz); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)

 $\delta$  191.3 (t,  $J_{\rm P-C}=$  19.1 Hz,  $C_{\alpha}$ ), 141.2–127.3 (Ph), 88.7 (Cp), 84.7 (CHPh), 81.2 (CPh(OMe)), 56.9 (CH<sub>3</sub>); MS (FAB, m/z) 944.3 (M<sup>+</sup> + 1), 682.1 (M<sup>+</sup> + 1 – PPh<sub>3</sub>), 429.0 (M<sup>+</sup> – PPh<sub>3</sub>, CNCHPhCPhC(OMe)O).

**Synthesis of 7g.** A mixture of complex **3c** (0.30 g, 0.37 mmol) and *N*,*N*-dimethylacetamide (0.05 mL, 0.5 mmol) in 40 mL of benzene was heated to reflux for 7 h. The workup procedure was the same as that for **7a**. Purification by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:5) gave **7g** (0.17 g, 54% yield). Spectroscopic data for **7g**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.49–7.31 (m, 35 H, Ph), 5.12 (s, 1H, CH), 4.77 (s, 5H, Cp), 2.46 (s, 6H, NMe<sub>2</sub>), 1.13 (s, 3H, Me); <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  51.8.0, 49.8 (AB, *J*<sub>P-P</sub> = 34.6 Hz); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  192.7 (t, *J*<sub>P-C</sub> = 19.4 Hz, C<sub>a</sub>), 137.9–126.5 (m, Ph), 89.1 (Cp), 86.9 (CHPh), 82.0 (CMe), 37.6 (N(CH<sub>3</sub>)<sub>2</sub>) 24.3 (CH<sub>3</sub>); MS (FAB, *m/z*) 894.2 (M<sup>+</sup> + 1), 632.1 (M<sup>+</sup> + 1 – PPh<sub>3</sub>), 429.0 (M<sup>+</sup> – PPh<sub>3</sub>, CNCHPhCMe(NMe<sub>2</sub>)O).

Synthesis of {[Ru]CNCHPhC(CH<sub>3</sub>)<sub>2</sub>OH}[PF<sub>6</sub>] (8a\*). A solution of 2c\* (0.22 g, 0.26 mmol), NaOMe (0.25 g, 4.5 mmol), and KPF<sub>6</sub> (0.15 g, 0.8 mmol) in acetone (20 mL) was stirred at room temperature for 2 days. The solvent was then removed under reduced pressure, the white residue was recrystallized from  $CH_2Cl_2$ /diethyl ether (1:10) to give suitable single crystals for diffraction analysis, and the product was identified as complex 8a\* (0.10 g, 38% yield). Spectroscopic data for 8a\*: IR (KBr) 2118 cm<sup>-1</sup> (s,  $\nu_{CN}$ ), 3576 cm<sup>-1</sup> (br,  $\nu_{OH}$ ); <sup>1</sup>H NMR (CDCl<sub>3</sub>) & 7.53-7.12 (m, 30H, Ph), 5.46 (s, 1H, CH), 2.67-2.27 (m, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.53 (s, 1H, OH), 1.39 (s, 15H, 5CH<sub>3</sub>), 1.26 (s, 3H, CH<sub>3</sub>), 1.27 (s, 3H, CH<sub>3</sub>); <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  38.44, 38.06 (AB,  $J_{\rm P-P}\,{=}\,46.5$  Hz); MS (FAB,  $m/\!z,\,{\rm Ru}^{102})\,824.3$  $(M^+)$ , 766.3  $(M^+ - CMe_2OH)$ . Anal. Calcd for  $C_{48}H_{54}F_6$ -NOP<sub>3</sub>Ru: C, 59.50; H, 5.58; N, 1.44. Found: C, 59.59; H, 5.44; N, 1.51.

Reduction of 7a by NaBH<sub>3</sub>CN in MeOH. To a solution of 7a (1.20 g, 1.38 mmol) in 30 mL of MeOH at room temperature was added NaBH<sub>3</sub>CN (0.11 g, 1.6 mmol). The mixture was stirred for 1 h, and the color changed from yellow to bright yellow. The solvent was removed under vacuum, and the solid residue was extracted with hexane. The extract was filtered through silica gel and the residue passed through a silica gel packed column to give 1 (0.88 g, 94%). The solvent of the filtrate was removed under vacuum to give PhCH<sub>2</sub>-CMe<sub>2</sub>OH (10a; 0.21 g, 96% yield). Spectroscopic data for 10a: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.24–7.04 (m, 5 H, Ph), 2.56 (s, 2H, CH<sub>2</sub>), 1.24 (s, 1H, OH), 1.04 (s, 6H, 2Me); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>)  $\delta$  138.5,

130.8, 128.3, 126.5 (Ph), 70.3 (COH), 50.0 (CMe), 29.3 (CH<sub>3</sub>); high-resolution MS (m/z) found 150.1041, calcd 150.2200. Anal. Calcd for C<sub>10</sub>H<sub>14</sub>O: C, 79.96; H, 9.39. Found: C, 79.91; H, 9.44.

X-ray Diffraction Analysis of 8a\* and 7a\*. Single crystals of 8a\* suitable for X-ray diffraction study were grown as mentioned above. A single crystal of dimensions  $0.30 \times 0.25$  $\times$  0.20  $mm^3$  was glued to a glass fiber and mounted on a SMART CCD diffractometer. The data were collected using Mo K $\alpha$  radiation (T = 295 K) from a sealed tube. Exposure time was 5 s per frame. SADABS<sup>34</sup> (Siemens area detector absorption) correction was applied, and decay was negligible. Data were processed, and the structures were solved and refined by the SHELXTL<sup>35</sup> program. The structure was solved using direct methods and confirmed by Patterson methods refining on  $F^2$  using all data.<sup>36</sup> Hydrogen atoms were placed geometrically using the riding model, with thermal parameters set to 1.2 times that for the atoms to which the hydrogen is attached and 1.5 times that for the methyl hydrogens. The procedures for the structure determination of  $7a^*$  were similar to those for 8a\*. Crystal data of these complexes are listed in Table 1.

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**Supporting Information Available:** Details of the structural determination for complexes **7a**\* and **8a**\*, including tables of crystal data and structure refinement, positional and anisotropic thermal parameters, and listings of bond distances and angles (CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

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<sup>(34)</sup> SAINT (Siemens Area Detector Integration) program; Siemens Analytical X-ray, Madison, WI, 1995.

<sup>(35) (</sup>a) The ŠADABS program is based on the method of Blessing; see: Blessing, R. H. Acta Crystallogr., Sect. A 1995, 51, 33-38. (b) SHELXTL: Structure Analysis Program, version 5.04; Siemens Industrial Automation Inc., Madison, WI, 1995.

<sup>(36)</sup> GOF =  $[\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$ , where *n* and *p* denote the number of data and parameters. R1 =  $(\sum||F_o| - |F_c||)/\sum|F_o|$ ; wR2 =  $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ , where  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$  and  $P = [(\max; 0, F_o^2) + 2F_c^2]/3$ .