

Preparation of Ruthenium Azirinyll Complexes and Reversed Regiospecificity of the Carbonyl Insertion Reaction

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Electrophilic addition of organic halides to [Ru]CN (**1**; [Ru] = Cp(PPh₃)₂Ru) gave the cationic isocyanide complexes {[Ru]CNCH₂R}X (R = CN, **2a**; R = CH=CH₂, **2b**; R = Ph, **2c**), which reacted with base (*n*-Bu₄NOH or *n*-Bu₄NF) to give the three-membered-ring azirinyll complexes. For the azirinyll complex with a phenyl group **3c**, three isomers, assigned as ruthenium *2H*- and *1H*-azirinyll complexes, are observed at -20 °C. Reaction of the methyl isocyanoacetate complex {[Ru]C≡NCH₂COOMe}X (**2d**) with *n*-Bu₄NOH 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 azirinyll 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*** and **8a*** 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.¹ The ring system occurs naturally with dysidazirine,² found as a constituent of marine sponges, and azirinomycin, an antibiotic isolated from *streptomyces aureus* cultures.³ Due to the asymmetry of the azirine there are two isomers, referred to as *1H*- and *2H*-azirine. The former, known only as a transient intermediate, represents a cyclic conjugated system with four π -electrons. The *2H*-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,⁴ although lower values of 44.6 and 46.7 kcal/mol have recently been reported.⁵ 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 *2H*-azirines may be a sign of polarization toward the more electronegative nitrogen atom.⁶ The corresponding values for the isoelectric cyclopropene ring are about 10 kcal/mol higher than for *2H*-azirine at the same levels of theory. Calculations showed that the azirinyll cation exhibited aromatic properties.⁷

(1) (a) Palacios, F.; Ochoa de Retana, A. M.; de Marigorta, E. M.; de los Santos, J. M. *Eur. J. Org. Chem.* **2001**, 2401–2414. (b) Gilchrist, T. L. *Aldrichim. Acta* **2001**, *34*, 51. (c) Ewing, D. F. In *Rodd's Chemistry of Carbon Compounds*, second supplements to the 2nd ed.; Sainsbury, M., Ed.; Elsevier Science: Amsterdam, 1997; Vol. IVA, pp 59–90. (d) Murphree, S. S.; Padwa, A. Three-Membered Ring Systems. In *Progress in Heterocyclic Chemistry*; Scriven, E. F. V., Suschitzky, H., Eds.; Pergamon Press: Oxford, U.K., 1997; Vol. 9, pp 43–63. (e) Pearson, W. H.; Lian, B. W.; Bergmeier, S. C.; Padwa, A. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon Press: Oxford, U.K., 1996; Vol. 1A, Chapter 1, pp 1–60. (f) Backes, J. *Methoden Org. Chem. (Houben-Weyl)* **1992**, *E16c*, 317–369. (g) Nair, V. In *The Chemistry of Heterocyclic Compounds*; Hassner, A., Ed.; Wiley: New York, 1983; Vol. 42, Part 1, Chapter 2, pp 215–332. (h) Liebman, J. F.; Greenberg, A. *Strained Organic Molecules*; Wiley: New York, 1978; p 91. (i) Fowler, F. W. *Adv. Heterocycl. Chem.* **1971**, *13*, 45–76.

(2) (a) Salomon, C. E.; Williams, D. H.; Faulkner, D. J. *J. Nat. Prod.* **1995**, *58*, 1463–1466. (b) Molinski, T. F.; Ireland, C. M. *J. Org. Chem.* **1988**, *53*, 2103–2105.

(3) Miller, T. W.; Tristram, E. W.; Wolf, F. J. *J. Antibiot.* **1971**, *24*, 48–55.

(4) Heimgartner, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 238–264.

(5) Calvo-Losada, S.; Quirante, J. J.; Suárez, D.; Sordo, T. L. *J. Comput. Chem.* **1998**, *19*, 912–922.

(6) Piquet, V.; Baccaredo, A.; Gornitzka, H.; Dahan, F.; Bertrand, G. *Chem. Eur. J.* **1997**, *3*, 1757–1764.

(7) (a) Alcamí, M.; Mó, O.; Yáñez, M. *J. Am. Chem. Soc.* **1993**, *115*, 11074–11083. (b) Lau, K.-C.; Li, W.-K.; Ng, C. Y.; Chiu, S.-W. *J. Phys. Chem. A* **1999**, *103*, 3330–3335. (c) Mayer, P. M.; Taylor, M. S.; Wong, M. W.; Radom, L. *J. Phys. Chem. A* **1998**, *102*, 7074–7080. (d) Banert, K.; Hagedorn, M.; Knözinger, E.; Becker, A.; Würthwein, E.-U. *J. Am. Chem. Soc.* **1994**, *116*, 60–62.

A number of general methods⁸ are available for the synthesis of organic 2*H*-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.⁹ It is known that photochemically induced reaction¹⁰ of azirines with ketone or aldehyde leads to isolation of oxazolines, whose metal complexes have been extensively used in metal-catalyzed enantioselective synthesis.¹¹ However, metal complexes containing azirinylligands 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 $-\text{CH}_2\text{R}$ group at C_β of the vinylidene ligand to give a metal complex containing a strained cyclopropenyl ligand.¹² 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.¹³ Therefore, we set out to explore deprotonation reactions of the cationic ruthenium isocyanide $[\text{Ru}]\text{C}\equiv\text{NCH}_2\text{R}^+$ system. The expected three-membered azirinylligand 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 azirinylligand obtained from ruthenium isocyanides is observed. Herein we report the preparation of the cationic ruthenium isocyanide complexes $[\text{Cp}(\text{LL}')\text{RuCNCH}_2\text{R}]\text{X}$ and subsequent deprotonation reaction and insertion of a carbonyl group into the azirinylligand.¹⁴

Results and Discussion

Synthesis of Isocyanide Complexes by Alkylation. Cationic isocyanide complexes are usually pre-

(8) (a) Padwa, A.; Carlsen, P. H. *J. Org. Chem.* **1978**, *43*, 2029–2037. (b) Nishiwaki, T. *Tetrahedron Lett.* **1969**, 2049–2052. (c) Singh, B.; Zweig, A.; Gallivan, J. B. *J. Am. Chem. Soc.* **1972**, *94*, 1199–1206. (d) Hassner, A.; Alexanian, V. *J. Org. Chem.* **1979**, *44*, 3861–3864.

(9) (a) Timen, A. S.; Fischer, A.; Somfai, P. *Chem. Commun.* **2003**, 1150–1151. (b) Padwa, A.; Woolhouse, A. D. In *Comprehensive Heterocyclic Chemistry I*; Katritzky, A. R., Rees, C. W., Lwowski, W., Eds.; Pergamon Press: Oxford, U.K., 1984; Vol. 7, Chapter 5, pp 47–93.

(10) Padwa, A. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum Press: New York, 1984; p 313.

(11) (a) Evans, D. A.; Miller, S. J.; Lectka, T. *J. Am. Chem. Soc.* **1993**, *115*, 6460–6461. (b) Bremberg, U.; Larhed, M.; Moberg, C.; Hallberg, A. *J. Org. Chem.* **1999**, *64*, 1082–1083. (c) Lightfoot, A.; Schnider, P.; Pfaltz, A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2897–2899. (d) Williams, J. M. J. *Synlett* **1996**, 705–710.

(12) (a) Ting, P. C.; Lin, Y. C.; Cheng, M. C.; Wang, Y. *Organometallics* **1994**, *13*, 2150–2152. (b) Ting, P. C.; Lin, Y. C.; Lee, G. H.; Cheng, M. C.; Wang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 6433–6444. (c) Chang, C. W.; Ting, P. C.; Lin, Y. C.; Lee, G. H.; Wang, Y. *J. Organomet. Chem.* **1998**, *553*, 417–425. (d) Lo, Y. H.; Lin, Y. C.; Lee, G. H.; Wang, Y. *Organometallics* **1999**, *18*, 982–988. (e) Lin, Y. C. *J. Organomet. Chem.* **2001**, *617–618*, 141–147. (f) Huang, C. C.; Lin, Y. C.; Huang, S. L.; Liu, Y. H.; Wang, Y. *Organometallics* **2003**, *22*, 1512–1518.

(13) (a) Chang, K.-H.; Lin, Y.-C. *Chem. Commun.* **1998**, 1441–1442. (b) Chang, K.-H.; Lin, Y.-C.; Liu, Y.-H.; Wang, Y. *Dalton* **2001**, 3154–3159.

(14) Yang, J. Y.; Lo, Y. H.; Huang, S. L.; Lin, Y. C. *Organometallics* **2001**, *20*, 3621–3623.

pared by direct ligand exchange.¹⁵ However, many free isocyanides of the type CNCH_2R 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,¹⁶ 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.¹⁷ We found that this preparative method is convenient to introduce alkyl or aryl groups to the ruthenium-coordinated cyanide ligand using various organic halides.

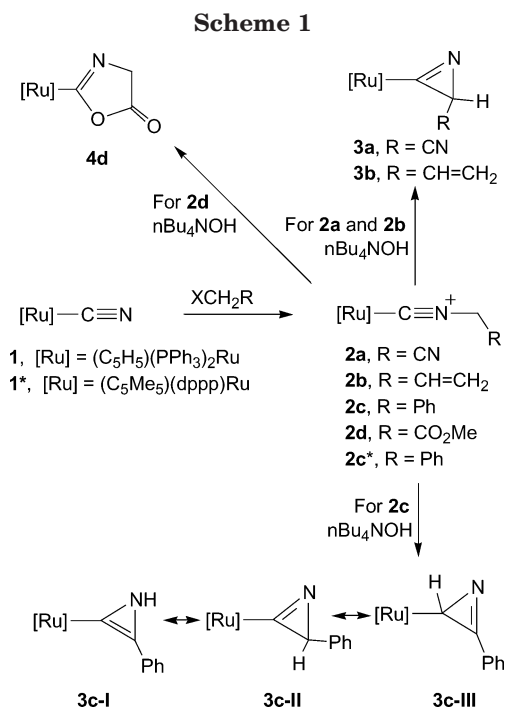
Treatment of **1** with excess bromoacetonitrile in CHCl_3 at reflux temperature afforded a green solution. Evaporation of the solvent under reduced pressure gave a green oil, which was then dissolved in a minimum amount of CH_2Cl_2 . Addition of this solution dropwise into vigorously stirred Et_2O caused the pale green solids to precipitate out. The solid was collected by filtration and washed with Et_2O to afford $\{[\text{Ru}]\text{C}\equiv\text{NCH}_2\text{CN}\}\text{Br}$ (**2a**; $[\text{Ru}] = \text{Cp}(\text{PPh}_3)_2\text{Ru}$) with 75% yield. Similarly, preparations of complexes $[\text{Ru}]\text{CNCH}_2\text{R}^+$ ($\text{R} = \text{CH}=\text{CH}_2$, **2b**; $\text{R} = \text{C}_6\text{H}_5$, **2c**; $\text{R} = \text{COOCH}_3$, **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_3 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 ^1H NMR spectrum of **2a** shows the expected methylene peak at δ 5.51. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, the singlet resonance at δ 45.4 is assigned to the PPh_3 ligand. In the ^1H NMR spectrum of **2d** in CDCl_3 , the singlet resonance at δ 4.92 is assigned to the methylene group of the isocyanide ligand, slightly shifted from that of **2a**. Two singlet resonances at δ 4.76 and 3.60 are assigned to the Cp and methyl groups, respectively. In the ^{13}C NMR spectrum of **2d** in CDCl_3 , the most characteristic spectroscopic data consist of a singlet resonance at δ 165.4 assigned to the carbonyl carbon, and the triplet resonance at δ 158.6 with $^2J_{\text{C}-\text{P}} = 20.2$ Hz is assigned to the ruthenium-bonded isocyanide carbon, symbolized here as C_α . The methyl and methylene resonances of the isocyanide ligand appear as two singlets at δ 52.5 and 47.8, respectively. The ^{31}P

(15) (a) Malatesta, L.; Bonati, F. *Isocyanide Complexes of Metals*; Wiley: London, 1969. (b) Schaal, M.; Beck, W. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 527–528. (c) Doonan, D. J.; Balch, A. L. *Inorg. Chem.* **1974**, *13*, 921–927. (d) Dozza, L.; Sutton, J. E.; Taube, H. *Inorg. Chem.* **1982**, *21*, 3997–4000. (e) Baird, G. J.; Davies, S. G. *J. Organomet. Chem.* **1984**, *262*, 215–221. (f) Albers, M. O.; Liles, D. C.; Robinson, D. J.; Singleton, E. *Organometallics* **1987**, *6*, 2179–2189. (g) Dussel, R.; Pilette, D.; Dixneuf, P. H.; Fehlhammer, W. P. *Organometallics* **1991**, *10*, 3287–3291.

(16) Cernák, J.; Orendác, M.; Potocnák, I.; Chomic, J.; Orendáčová, A.; Skorsepa, J.; Feher, A. *Coord. Chem. Rev.* **2002**, *224*, 51–66.

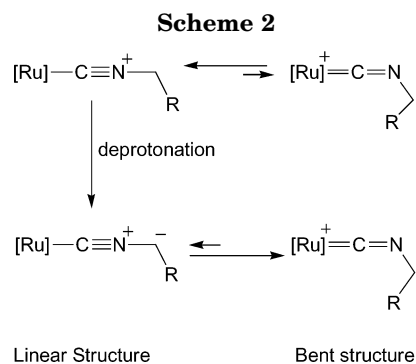
(17) (a) Michelin, R. A.; Pombeiro, A. J. L.; Guedes da Silva, M. F. C. *Coord. Chem. Rev.* **2001**, *218*, 75–112. (b) Lentz, D.; Röttger, M. *J. Organomet. Chem.* **1999**, *592*, 41–45. (c) Kunz, R.; Fehlhammer, W. P. *Angew. Chem.* **1994**, *106*, 331–332. (d) Fehlhammer, W. P.; Degel, F.; Beck, G. *Chem. Ber.* **1987**, *120*, 461–469. (e) Bae, E.; Völkl, A.; Beck, F.; Fehlhammer, W. P.; Robert, A. *J. Chem. Soc., Dalton Trans.* **1986**, 863–868.



NMR spectrum of **2d** displays a singlet resonance at δ 46.0 in CDCl_3 . 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_3 and both PPh_3 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 $[\text{Ru}^*]\text{CN}$ ($[\text{Ru}^*] = (\eta^5\text{-C}_5\text{Me}_5)(\text{dppp})\text{Ru}$, **1***) with PhCH_2Br affords the cationic isocyanide complex $\{[\text{Ru}^*]\text{CNCH}_2\text{Ph}\}\text{Br}$ (**2c***) in high yield. In the ^{13}C NMR spectrum of **2c***, the triplet resonance at δ 160.65 with $J_{\text{P-C}} = 19.4$ Hz is assigned to C_α . The C_α resonance of the previously reported ruthenium isocyanide compound $\text{Cp}^*\text{Ru}(\text{CN})(\text{CN}^t\text{Bu})(\text{Ppyl}_3)$, ($\text{Ppyl}_3 = \text{tripyrrolylphosphine}$) was found at δ 155.6 as a doublet with $J_{\text{P-C}} = 25.8$ Hz in the ^{13}C NMR spectrum.¹⁸

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 electron-withdrawing 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 azirinyne complex **3a** (see Scheme 1) when **2a** in CH_2Cl_2 is treated with a solution of $n\text{-Bu}_4\text{NOH}$ 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 ^{31}P NMR resonance at δ 45.4 for **2a** is converted to two doublet resonances at δ 49.1 and 48.7 with $J_{\text{P-P}} = 34.8$ Hz, clearly indicating the formation of an azirinyne ring containing a stereogenic carbon center. In the ^{13}C NMR



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

Similarly, deprotonation of $\{[\text{Ru}]\text{CNCH}_2\text{CH}=\text{CH}_2\}^+$ (**2b**) by $n\text{-Bu}_4\text{NF}$ at 0°C in CH_2Cl_2 affords the azirinyne complex **3b** in 88% yield. Use of DBU or $n\text{-Bu}_4\text{NOH}/\text{MeOH}$, instead of $n\text{-Bu}_4\text{NF}$, gives several unidentifiable complexes along with **3b** as a minor product. In the ^{31}P NMR spectrum of **3b** the two-doublet pattern, i.e., resonances at δ 52.0 and 48.8 with $J_{\text{P-P}} = 34.8$ Hz, is consistent with the presence of a stereogenic center. In the ^1H NMR spectrum of **3b** three multiplet resonances at δ 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 δ 5.73 assignable to the internal $=\text{CH}$, as compared to the ddt coupling pattern of the resonance at δ 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 δ 2.76 is assigned to the proton on the azirinyne ring. Again addition of protic acid to **3b** yields **2b**.

In contrast to the metal vinylidene system with a bent structure at C_β , 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 azirinyne ring.²⁰ This reaction is analogous to the facile deprotonation-induced cyclopropanation of the cationic ruthenium vinylidene system. In the vinylidene complex, the bent structure at C_β could assist formation of the cyclopropenyl ligand.²¹ It has been stressed that nitrile ylides, generated from the photolysis of *2H*-azirines, may be classified as nitrilium betaines, a class of 1,3-dipoles containing a

(19) Banert, K.; Hagedorn, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 103–105.

(20) (a) Yamamoto, Y. *Coord. Chem. Rev.* **1980**, *32*, 193–233. (b) Singleton, E.; Oosthuizen, H. E. *Adv. Organomet. Chem.* **1983**, *22*, 209–310. (c) Carnahan, E.; Lippard, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 3230–3231. (d) Aharonian, G.; Hubert-Pfalzgraf, L. G.; Zaki, A.; Le Borgne, G. *Inorg. Chem.* **1991**, *30*, 3105–3107.

(21) (a) Beckhaus, R. *J. Chem. Soc., Dalton Trans.* **1997**, 1991–2002. (b) Bruneau, C.; Dixneuf, P. H. *Acc. Chem. Res.* **1999**, *32*, 311–323. (c) Bustelo, E.; Carbo, J. J.; Lledos, A.; Mereiter, K.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **2003**, *125*, 3311–3321. (d) Adams, C. J.; Pope, S. J. A. *Inorg. Chem.* **2004**, *43*, 3492–3499.

(18) Rodrigurz, V.; Donnadiou, B.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1998**, *17*, 3809–3814.

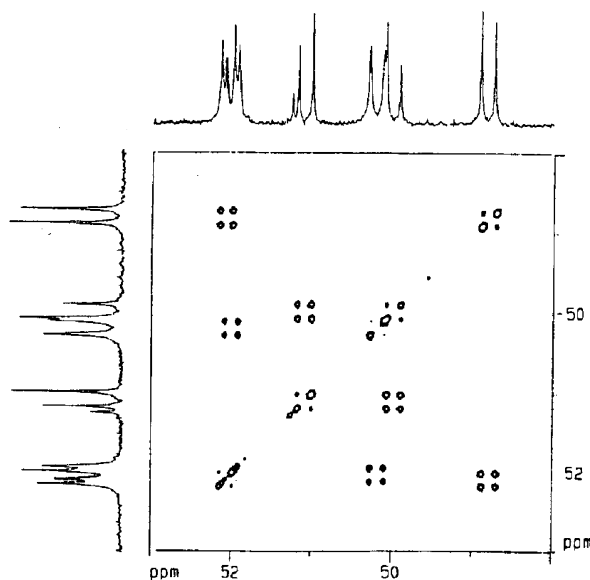


Figure 1. 2D ^{31}P NMR spectrum of complex **3c**, revealing the presence of three isomers.

central nitrogen and a π bond orthogonal to the 4π 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.²²

Three Isomers of the Phenylazirinyl Complex.

Deprotonation of $\{[\text{Ru}]\text{CNCH}_2\text{Ph}\}\text{Br}$ (**2c**) in CH_2Cl_2 by $n\text{-Bu}_4\text{NOH}$ at 0°C also affords, in high yield, the thermally unstable azirinyl complex **3c** along with $[\text{Ru}]\text{CN}$ (**1**) as a minor product (ca. 5%). Use of other bases such as DBU and $n\text{-Bu}_4\text{NF}$ in THF also gave similar products, but with lower yield. The ^{31}P NMR spectrum of **3c** at -20°C displays three sets of doublet of doublets patterns at δ 51.98, 48.82, δ 51.89, 49.72, and δ 51.17, 50.15 in a ratio of approximately 2:2:3. The 2D ^{31}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 $2H$ -azirinyl complexes (Scheme 1), with one of them being thermodynamically more stable. The ^1H NMR spectrum at -20°C displaying three Cp singlet resonances at δ 4.59, 4.58, and 4.57 also in a ratio of 3:2:2, respectively, is consistent with the ^{31}P NMR data. Two ^1H NMR resonances at δ 4.89 and 4.71 are assigned to the CH groups, and the broad resonance at δ 3.23 is assigned to the NH group. Addition of D_2O to the solution of **3c** at -20°C causes immediate disappearance of the resonance at δ 3.23, confirming this assignment. This is followed by slow vanishing of the resonances at δ 4.89 and 4.71, indicating the presence of exchange processes between these three isomers. At -29°C the species with ^{31}P resonances at δ 51.17 and 50.15 and ^1H resonance at δ 3.23 disappears first. Then at -40°C only one isomer with ^{31}P resonances at δ 51.89 and 49.72 and ^1H resonance at δ 4.71 was observed. Attempts to obtain

^{13}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 $\{[\text{Ru}]\text{CNCH}_2\text{C}_6\text{H}_4\text{CN}\}\text{Br}$ (**2c'**) with base yielded 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_γ (the methylene group) of the isocyanide ligand is required in order to see three azirinyl isomers. Even though free $1H$ -azirine is considered as the least stable isomer in a pure organic system, the three-membered ring of the metalated $1H$ -azirine at one of the sp^2 carbons (**3c-II**) could significantly be stabilized by participation of metal d orbitals, thus making **3c-III** the least stable among the three.²³

Hydrolysis of the Isocyanide Complex with an Ester Group.

Treatment of $\{[\text{Ru}]\text{C}\equiv\text{NCH}_2\text{CO}_2\text{CH}_3\}\text{I}$, (**2d**) in acetone with $n\text{-Bu}_4\text{NOH}$ 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 δ 50.5 in the ^{31}P NMR spectrum, and in the ^1H NMR spectrum the 5:2 ratio for the two singlet resonances at δ 4.69 and 4.13, assignable to the Cp and CH_2 groups, is consistent with the formula. In the FAB mass spectrum, a parent peak at m/z 776.2 attributed to $(\text{M} + 1)^+$ is observed.²⁴ We previously reported the deprotonation reaction of a cationic vinylidene complex containing a methyl ester group at C_γ , i.e. $[\text{Ru}]=\text{C}(\text{Ph})\text{CH}_2\text{CO}_2\text{R}^+$, 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.

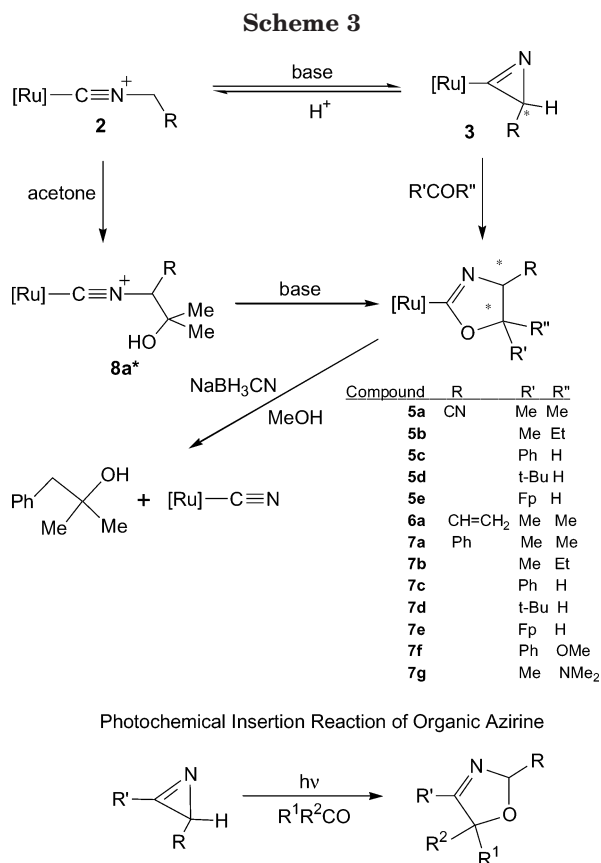
Transition-metal-induced reactions of azirine have been reported in a few cases. Initial 1,3-bond cleavage and generation of a nitrene–iron carbonyl complex as an intermediate was proposed in the reaction of azirine with diiron nonacarbonyls to give diimine complexes and urea diiron complexes.²⁵ Cycloaddition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

(23) MO calculations show $1H$ -azirine to be approximately 30 kcal less stable than $2H$ -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 $\text{Cp}(\text{PH}_3)_2\text{Ru}(\text{CNCHPh})$ (**3c'-I**, **3c'-II**, **3c'-III**) and found that **3c-I** is the most stable one among the possible isomers.

(24) (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.

(25) (a) Alper, H.; Prickett, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 191–192. (b) Inada, A.; Heimgartner, H.; Schmid, H. *Tetrahedron Lett.* **1979**, 2983–2986. (c) Alper, H.; Prickett, J. E. *Tetrahedron Lett.* **1976**, 2589–2590. (d) Isomura, K.; Uto, K.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1977**, 664–665.

(22) (a) Strauch, H. C.; Wibbeling, B.; Fröhlich, R.; Erker, G.; Jacobsen, H.; Berke, H. *Organometallics* **1999**, *18*, 3802–3812. (b) Gómex, M.; Martínezde Ilarduya, J. M.; Royo, P. J. *J. Organomet. Chem.* **1989**, *369*, 197–204.



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

Insertion of a Carbonyl Group into the Azirine Ring. The reaction of **2a** with $n\text{-Bu}_4\text{NOH}/\text{MeOH}$ in acetone, instead of CH_2Cl_2 , 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 azirine ring with C–C bond formation occurring at the sp^3 carbon of the azirine ring satisfactorily accounts for the formation of **5a**. Complex **5a** with a five-membered-ring ligand is more stable than that of **3a**. The ^{31}P NMR spectrum of **5a** displays two doublet resonances at δ 50.0 and 51.0 with $J_{\text{P-P}} = 34.5$ Hz, consistent with the presence of a stereogenic carbon center in the oxazolinyl ring. In the ^{13}C NMR spectrum of **5a**, the triplet resonance of C_α at δ 197.6 with $J_{\text{C-P}} = 18.8$ 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 ^{31}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 azirine and the oxazolinyl rings. In the ^1H NMR spectrum of the crude product, two pairs of two-doublet resonances at δ 4.53, 4.15 and δ 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 $^3J_{\text{H-H}}$ coupling. The C–C bond formation is thus believed to take place at the sp^3 carbon of the azirine 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 regioselective.²⁷ In the photoinduced addition reaction, the C–C bond formation takes place at the sp^2 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 derivatives or amino alcohols, which could be easily prepared by the reduction of α -amino acids, although other procedures are also used because of some particularly sensitive functionalities present on the precursors.²⁸

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_3CCHO only one diastereoisomer of **5d** was isolated. The carbonyl group on the coordinated Cp ligand of $\text{CpFe}(\text{C}_5\text{H}_4\text{CHO})$ 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 azirine ring has been reported, and CO_2 can also be replaced by ketone, aldehyde, or other carbonyl-containing compounds.²⁹

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

(27) (a) Clause, P.; Gilgen, P.; Hansen, H. J.; Heimgartner, H.; Jackson, B.; Schmid, H. *Helv. Chim. Acta* **1974**, *57*, 2173–2193. (b) Orahovats, A.; Jackson, B.; Heimgartner, H.; Schmid, H. *Helv. Chim. Acta* **1973**, *56*, 2007–2011.

(28) (a) Minakata, S.; Nishimura, M.; Takahashi, T.; Oderaotoshi, Y.; Komatsu, M. *Tetrahedron Lett.* **2001**, *42*, 9019–9022. (b) Kamata, K.; Agata, I.; Meyers, A. I. *J. Org. Chem.* **1998**, *63*, 3113–3116. (c) Ager, D. J.; Prakash, I.; Schaad, D. R. *Chem. Rev.* **1996**, *96*, 835–876. (d) Lafarge, P.; Guenot, P.; Lellouche, J.-P. *Heterocycles* **1995**, *41*, 947–958. (e) Rieger, D.; Lotz, S. D.; Kernbach, U.; Andre, C.; Bertran-Nadal, J.; Fehlhammer, W. P. *J. Organomet. Chem.* **1995**, *491*, 135–152. (f) Gant, T. G.; Meyers, A. I. *Tetrahedron* **1994**, *50*, 2297–2360. (g) Leonard, W. R.; Romine, J. L.; Meyers, A. I. *J. Org. Chem.* **1991**, *56*, 1961–1963. (h) Reuman, M.; Meyers, A. I. *Tetrahedron* **1985**, *41*, 837–860. (i) Meyers, A. I.; Mihelich, E. D. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 270–281. (j) Frump, J. A. *Chem. Rev.* **1971**, *71*, 483–505.

(29) (a) Orahovats, A.; Heimgartner, H.; Schmid, H.; Heintzelmann, W. *Helv. Chim. Acta* **1974**, *54*, 2626–2633. (b) Padwa, A.; Wetmore, S. I., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2414–2421. (c) Padwa, A.; Wetmore, S. I., Jr. *Org. Photochem. Synth.* **1976**, *2*, 87–95.

(26) Alper, H.; Wollowitz, S. *J. Am. Chem. Soc.* **1975**, *97*, 3541–3543.

Table 1. Crystal and Intensity Collection Data for Cp*(dppp)Ru[CNCHPhC(Me)₂O] (7a*) and Cp*(dppp)Ru[CNCHPhC(Me)₂OH][PF₆] (8a*)

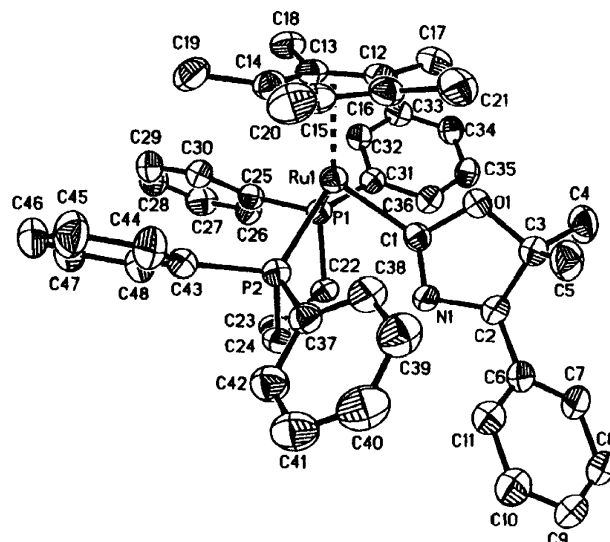
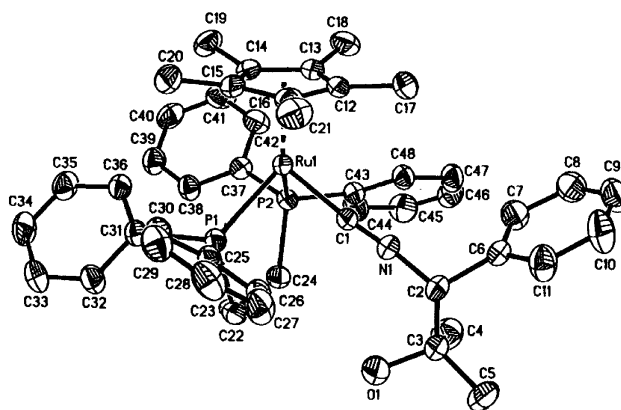
	7a*	8a*
mol formula	C ₅₄ H ₆₇ NOP ₂ Ru	C ₄₉ H ₅₄ NO ₂ P ₃ F ₆ Ru
mol wt	909.10	996.91
space group	<i>Pbca</i>	<i>P1</i>
<i>a</i> , Å	15.8700(3)	11.2850(2)
<i>b</i> , Å	18.9940(3)	13.8970(2)
<i>c</i> , Å	32.5140(8)	16.0390(3)
α, deg	90.00	78.8460(10)
β, deg	90.00	83.4930(10)
γ, deg	90.00	75.9960(10)
<i>V</i> , Å ³	9800.9(3)	2388.65(7)
<i>Z</i>	8	2
cryst dimens, mm ³	0.25 × 0.20 × 0.20	0.30 × 0.25 × 0.20
Mo Kα radiation, Å		0.710 73
θ 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/params	8022/0/485	8401/2/558
GOF	2.130	1.332
final <i>R</i> indices (<i>I</i> > 2σ(<i>I</i>))	R1 = 0.0711, wR2 = 0.1785	R1 = 0.0521, wR2 = 0.1529
<i>R</i> indices (all data)	R1 = 0.1095, wR2 = 0.2140	R1 = 0.0631, wR2 = 0.1674
Δδ (in final map), e/Å ³	−1.27, +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 oxazolonyl 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*-Bu₄NOH in acetone affords **7a***, a product resulting from addition of acetone after deprotonation of **2c***, in 60% yield. In the ¹H NMR spectrum of **7a***, the ¹H singlet peak at δ 4.94 is assigned to CHPh of the oxazolonyl ring. Two inequivalent methyl groups of **7a*** appear as two singlet resonances at δ 1.53 and 0.82. The characteristic C_α resonance in the ¹³C NMR spectrum of **7a*** appears as a doublet of doublets at δ 193.7 with coupling constants of *J*_{P–C} = 18.8 and 17.7 Hz. The ³¹P NMR spectrum of **7a*** displays two well-separated doublet resonances at δ 52.94 and 45.35 with *J*_{P–P} = 51.1 Hz.

However, treatment of **2c*** with NaOMe in the presence of KPF₆ in acetone solution affords [Ru*]CNCHPhC(Me)₂OH⁺ (**8a***) in 38% yield. In the IR spectrum of **8a***, the absorption peak at 2118 cm^{−1} is assigned to ν_{C=N} stretching and the broad peak at 3576 cm^{−1} is assigned to ν_{OH}. In the ¹H NMR spectrum of **8a***, two ¹H singlet peaks at δ 5.46 and 2.53 are assigned to the CHPh and the OH absorptions, respectively, with the latter readily vanishing in the presence of D₂O. The ³¹P NMR spectrum of **8a*** displaying AB type resonances at δ 38.44 and 38.06 with *J*_{P–P} = 46.5 Hz differs significantly from that of **7a***.

**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*** and **8a*** 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.³⁰ The Ru(1)–C(1) distance of **7a*** (2.054(5) Å) is slightly longer than the corresponding Ru(1)–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 oxazolonyl ring confirms the regioselective 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

(30) (a) Nishiyama, H.; Niwa, E.; Inoue, T.; Ishima, Y.; Aoki, K. *Organometallics* **2002**, *21*, 2572–2574. (b) Braunstein, P.; Naud, F.; Dedieu, A.; Rohmer, M. M.; DeCian, A.; Rettig, S. J. *Organometallics* **2001**, *20*, 2966–2981.

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_α of the oxazolonyl ring in **7a**.³¹ Treatment of **7a** with NaBH_3CN in MeOH afforded the organic alcohol $\text{PhCH}_2\text{CMe}_2\text{OH}$ and **1** in greater than 90% yield. Two products were separated by column chromatography. In the presence of D_2O the reaction gave $\text{PhCH}_2\text{CMe}_2\text{OD}$, $\text{NCC}_6\text{H}_4\text{CH}_2\text{CMe}_2\text{OH}$ and $\text{F}_3\text{CC}_6\text{H}_4\text{PhCH}_2\text{CMe}_2\text{OH}$ were also prepared from the corresponding complexes. The reaction in 0.1 g scale also occurred in hexane with slightly lower yield.³²

Concluding Remarks. We prepared ruthenium aziriny complexes by deprotonation reactions of ruthenium isocyanide complexes. In the ruthenium coordinated aziriny system with a phenyl substituent three isomers, including a 1*H*-aziriny complex, could be observed by NMR spectroscopy. Facile insertion of a carbonyl group of ketone, aldehyde, ester, and amide into the ruthenium-bound aziriny ring to give oxazolonyl complexes followed a different regioselectivity 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.

(31) (a) Davies, D.; Fawcett, J.; Garratt, S. A.; Russell, D. R. *Organometallics* **2001**, *20*, 3029–3034. (b) Glos, M.; Reiser, O. *Org. Lett.* **2000**, *2*, 2045–2048. (c) Schinnerl, M.; Seitz, M.; Kaiser, A.; Reiser, O. *Org. Lett.* **2001**, *3*, 4259–4262. (d) Gosh, A. K.; Mathivanan, P.; Capiello, J. *Tetrahedron: Asymmetry* **1998**, *9*, 1–45. (e) Jørgensen, K. A.; Johannsen, M.; Yao, S. L.; Audrain, H.; Thorhaug, J. *Acc. Chem. Res.* **1999**, *32*, 605–613. (f) Pfaltz, A. *Synlett* **1999**, 835–842. (g) Pfaltz, A. *J. Heterocycl. Chem.* **1999**, *36*, 1437–1451. (h) Johnson, J. S.; Evans, D. A. *Acc. Chem. Res.* **2000**, *33*, 325–335. (i) Fache, F.; Schulz, E.; Tommasino, M. L.; Lemaire, M. *Chem. Rev.* **2000**, *100*, 2159–2232.

(32) (a) Hon, Y.-S.; Lee, C.-F.; Chen, R.-J.; Szu, P.-H. *Tetrahedron* **2001**, *57*, 5991–6001. (b) Orita, A.; Tanahashi, C.; Kakuda, A.; Otera, J. *J. Org. Chem.* **2001**, *66*, 8926–8934. (c) Alonso, E.; Guijarro, D.; Martinez, P.; Ramon, D. J.; Yus, M. *Tetrahedron* **1999**, *55*, 11027–11038.

Experimental Section

General Procedures. All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. CH_2Cl_2 was distilled from CaH_2 , 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 δ with residual protons in the solvents as a reference (CDCl_3 , δ 7.24; $\text{C}_2\text{D}_6\text{O}$, δ 2.04). FAB mass spectra were recorded on a JEOL SX-102A spectrometer. Complexes $[\text{Ru}]\text{C}\equiv\text{N}$ (**1**; $[\text{Ru}] = (\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Ru}$) and $[\text{Ru}^*]\text{C}\equiv\text{N}$ (**1***; $[\text{Ru}^*] = (\eta^5\text{-C}_5\text{Me}_5)(\text{dppp})\text{Ru}$)³³ 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 $\{[\text{Ru}]\text{CNCH}_2\text{CN}\}\text{Br}$ (2a**).** To a sample of **1** (3.00 g, 4.18 mmol) dissolved in 70 mL of CHCl_3 at room temperature was added BrCH_2CN (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_2Cl_2 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**: ^1H NMR (CDCl_3) δ 7.32–7.05 (m, 30H, Ph), 5.51 (s, 2H, CH_2), 4.86 (s, 5H, Cp); ^{13}C NMR (CDCl_3) δ 165.1 (t, $J_{\text{C-P}} = 19.9$ Hz, C_α), 135.3–127.5 (Ph), 111.8 (CN), 88.4 (Cp), 35.4 (CH_2); ^{31}P NMR (CDCl_3) δ 45.4; MS (FAB, m/z , Ru^{102}) 757 (M^+), 495 ($\text{M}^+ - \text{PPh}_3$). Anal. Calcd for $\text{C}_{44}\text{H}_{37}\text{N}_2\text{P}_2\text{BrRu}$: C, 63.16; H, 4.46; N, 3.35. Found: C, 63.31; H, 4.59; N, 3.40.

Other isocyanide complexes $\{[\text{Ru}]\text{CNCH}_2\text{R}\}\text{X}$ ($\text{R} = \text{CH} = \text{CH}_2$, **2b**, 90% yield; $\text{R} = \text{C}_6\text{H}_5$, **2c**, 92% yield; $\text{R} = \text{COOCH}_3$, **2d**, 74% yield) were prepared similarly from the reactions of **1** with $\text{ICH}_2\text{CH}=\text{CH}_2$, $\text{BrCH}_2\text{C}_6\text{H}_5$, and $\text{BrCH}_2\text{COOCH}_3$, respectively. Spectroscopic data for **2b**: ^1H NMR (CDCl_3) δ 7.36–7.04 (m, 30H, Ph), 5.59 (ddt, $J_{\text{H-H}} = 15.4, 10.0, 7.2$ Hz, 1H, $=\text{CH}$), 5.16 (d, $J_{\text{H-H}} = 15.4$ Hz, 1H, $=\text{CH}$), 5.09 (d, $J_{\text{H-H}} = 10.0$ Hz, 1H, $=\text{CH}$), 4.79 (s, 5H, Cp), 4.57 (d, $J_{\text{H-H}} = 7.2$ Hz, CH_2); ^{13}C NMR (CDCl_3) δ 153.0 (t, $J_{\text{C-P}} = 21.0$ Hz, C_α), 135.8–128.3 (Ph), 129.3 (CH), 118.9 (CH_2), 87.6 (Cp), 49.2 (CH_2); ^{31}P NMR (CDCl_3) δ 46.3; MS (FAB, m/z , Ru^{102}) 758 (M^+), 496 ($\text{M}^+ - \text{PPh}_3$), 429 ($\text{M}^+ - \text{PPh}_3 - \text{CNC}_3\text{H}_5$). Anal. Calcd for $\text{C}_{45}\text{H}_{40}\text{NP}_2\text{IRu}$: C, 61.09; H, 4.56; N, 1.58. Found: C, 61.15; H, 4.64; N, 1.49. Spectroscopic data for **2c**: ^1H NMR (CDCl_3) δ 7.34–6.92 (m, 30H, Ph), 5.11 (s, 2H, CH_2), 4.77 (s, 5H, Cp); ^{31}P NMR (CDCl_3) δ 45.4; MS (FAB, m/z , Ru^{102}) 808 (M^+), 546 ($\text{M}^+ - \text{PPh}_3$). Anal. Calcd for $\text{C}_{49}\text{H}_{42}\text{NP}_2\text{BrRu}$: C, 66.29; H, 4.77; N, 1.58. Found: C, 66.25; H, 4.83; N, 1.62. Spectroscopic data for **2d**: ^1H NMR (CDCl_3) 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}C NMR (CDCl_3) δ 165.4 ($\text{C}=\text{O}$), 158.2 (t, $J_{\text{C-P}} = 20.2$ Hz, C_α), 135.5–127.6 (Ph), 87.7 (Cp), 52.5 (CH_2), 47.8 (CH_3); ^{31}P NMR (CDCl_3) δ 46.0; MS (FAB, m/z , Ru^{102}) 790 (M^+), 528 ($\text{M}^+ - \text{PPh}_3$). Anal. Calcd for $\text{C}_{45}\text{H}_{40}\text{NO}_2\text{P}_2\text{BrRu}$: C, 62.14; H, 4.64; N, 1.61. Found: C, 62.39; H, 4.89; N, 1.70.

Synthesis of $\{[\text{Ru}^*]\text{CNCH}_2\text{Ph}\}\text{Br}$ (2c***).** To a Schlenk flask charged with $[\text{Ru}^*]\text{CN}$ (**1***; 0.20 g, 0.30 mmol) and CHCl_3 (40 mL) was added BrCH_2Ph (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 $\text{CH}_2\text{Cl}_2/n$ -hexane (1:10) and was identified as **2c*** (0.14

(33) (a) Baird, G. J.; Davies, S. G.; Moon, S. D.; Simpson, S. J.; Jones, R. H. *J. Chem. Soc., Dalton Trans.* **1985**, 1479–1486. (b) Laidlaw, W. M.; Denning, R. G. *J. Organomet. Chem.* **1993**, *463*, 199–204.

g, 57% yield). Spectroscopic data for **2c***: IR (KBr) 2115 cm^{-1} (s, ν_{CN}); ^1H NMR (CDCl_3) δ 7.42–7.08 (m, 30H, Ph), 5.18 (s, 2H, CH_2), 2.59–1.52 (m, 6H, CH_2), 1.34 (s, 15H, 5 CH_3); ^{13}C NMR (CDCl_3) δ 160.6 (t, $J_{\text{P-C}} = 19.4$ Hz, CN), 136.1–128.1 (Ph), 96.6 (s, Cp), 50.1 (s, CH_2), 30.4 (t, $J_{\text{P-C}} = 17.5$ Hz, CH_2), 20.9 (s, CH_2), 9.7 (s, 5 CH_3). ^{31}P NMR (CDCl_3) δ 37.80; MS (FAB, m/z , Ru^{102}) 766.3 (M^+), 649.3 ($\text{M}^+ - \text{CNCH}_2\text{Ph}$). Anal. Calcd for $\text{C}_{45}\text{H}_{48}\text{N}_2\text{RuBr}$: 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_2Cl_2 at 0 $^\circ\text{C}$ was added a solution of *n*-Bu₄NOH (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 $^\circ\text{C}$ 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**: ^1H NMR (CD_3CN , –20 $^\circ\text{C}$) δ 7.63–7.18 (m, 30H, Ph), 4.26 (s, 5H, Cp), 2.98 (s, 1H, CH); ^{13}C NMR (CD_3CN , –20 $^\circ\text{C}$) δ 184.3 (t, $J_{\text{P-C}} = 19.9$ Hz, C_α), 138.1–127.3 (Ph), 119.3 (CN), 88.9 (Cp), 11.3 (CH); ^{31}P NMR (CD_3CN , –20 $^\circ\text{C}$) δ 49.1, 48.7 (2d, $J_{\text{P-P}} = 34.8$ Hz). MS (FAB) m/z : 757.3 ($\text{M}^+ + 1$), 495.0 ($\text{M}^+ + 1 - \text{PPh}_3$), 429.0 ($\text{M}^+ + 1 - \text{PPh}_3$, 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_2Cl_2 at 0 $^\circ\text{C}$ was added a THF solution of *n*-Bu₄NF. The mixture was stirred for 10 min, and the color changed to bright yellow. Then the solvent was removed under vacuum at 0 $^\circ\text{C}$ 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**: ^1H NMR (C_6D_6 , 10 $^\circ\text{C}$) δ 7.42–7.06 (m, 30H, PPh₃), 5.73 (ddd, $J_{\text{H-H}} = 18.2$, 9.1, 7.2 Hz, 1H, =CH), 5.26 (d, $J_{\text{H-H}} = 18.2$ Hz, 1H, =CH), 5.21 (d, $J_{\text{H-H}} = 9.1$ Hz, 1H, =CH), 4.73 (s, 5H, Cp), 2.76 (d, $J_{\text{H-H}} = 7.2$ Hz, 1H, CNCH); ^{31}P NMR (C_6D_6 , 10 $^\circ\text{C}$) δ 52.0, 48.8 (AB, $J_{\text{P-P}} = 34.8$ Hz); MS (FAB, m/z) 758.2 ($\text{M}^+ + 1$), 496.1, ($\text{M}^+ + 1 - \text{PPh}_3$), 429.0 ($\text{M}^+ + 1 - \text{PPh}_3$, CNCH=CH₂).

Reaction of $\{[\text{Ru}]\text{CNCH}_2\text{C}_6\text{H}_5\}\text{Br}$ with *n*-Bu₄NOH. To a solution of **2c** (0.14 g, 0.16 mmol) in 20 mL of acetone was added a solution of *n*-Bu₄NOH (0.5 mL) at 0 $^\circ\text{C}$. 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 $^\circ\text{C}$. The extract was filtered through Celite. The solvent of the filtrate was removed under vacuum at 0 $^\circ\text{C}$ to give the products **3c** (0.12 g, 95% yield). Three isomers are observed in the spectra of **3c** at –20 $^\circ\text{C}$. Spectroscopic data for **3c**: ^1H NMR ($\text{C}_6\text{D}_5\text{CD}_3$ at –20 $^\circ\text{C}$) 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); ^{31}P NMR ($\text{C}_6\text{D}_5\text{CD}_3$ at –20 $^\circ\text{C}$) δ 51.98, 48.82 (2d, $J_{\text{P-P}} = 34.8$ Hz), 51.89, 49.72 (2d, $J_{\text{P-P}} = 34.8$ Hz), 51.17, 50.15 (2d, $J_{\text{P-P}} = 34.9$ Hz); MS (FAB of the mixture, m/z) 808.4 ($\text{M}^+ + 1$), 546.2 ($\text{M}^+ + 1 - \text{PPh}_3$), 429.0 ($\text{M}^+ + 1 - \text{PPh}_3$, CNCH₂Ph); high-resolution MS (FAB, m/z) calcd for $\text{C}_{49}\text{H}_{42}\text{RuP}_2\text{N}$ ($\text{M}^+ + 1$) 808.1850, found 808.1836. Complex **3c** in pure form was not obtained. Variable-temperature NMR data were collected in $\text{C}_6\text{D}_5\text{CD}_3$, and at –40 $^\circ\text{C}$ only one isomer is observed.

Reaction of 2d with *n*-Bu₄NOH. To a solution of **2d** (0.14 g, 0.16 mmol) in 20 mL of acetone was added a solution of *n*-Bu₄NOH (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**: ^1H NMR (CDCl_3) δ 7.65–7.00 (m, 30H, Ph), 4.69 (s, 5H,

Cp), 4.13 (s, 2H, CH_2); ^{31}P NMR (CD_3COCD_3) δ 50.5; MS (FAB, m/z) 776.2 ($\text{M}^+ + 1$), 514.0 ($\text{M}^+ + 1 - \text{PPh}_3$), 428.9 ($\text{M}^+ + 1 - \text{PPh}_3$, CNCH₂CO₂).

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*-Bu₄NOH (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**: ^1H NMR (C_6D_6) δ 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); ^{13}C NMR (C_6D_6) δ 197.6 (t, $J_{\text{P-C}} = 18.8$ Hz, C_α), 140.4–127.4 (Ph), 119.2 (CN), 86.3 (Cp), 79.5 ($\text{C}(\text{Me})_2$), 68.2 (CH), 27.8 (CH_3), 25.3 (CH_3); ^{31}P NMR (CDCl_3) δ 51.0, 50.0 (AB, $J_{\text{P-P}} = 34.5$ Hz); MS (FAB, m/z) 815.3 ($\text{M}^+ + 1$), 553.1 ($\text{M}^+ + 1 - \text{PPh}_3$), 429.0 ($\text{M}^+ + 1 - \text{PPh}_3 - \text{CNCHCN}(\text{CH}_3)_2\text{O}$). Anal. Calcd for $\text{C}_{47}\text{H}_{42}\text{N}_2\text{OP}_2\text{Ru}$: 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*-Bu₄NOH (0.5 mL) in 20 mL of CH_2Cl_2 at room temperature. A mixture containing two diastereomers (5:4) was isolated. Spectroscopic data for **5b**: ^1H NMR (CDCl_3 , major product) δ 7.62–7.00 (m, 30 H, PPh₃), 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_2CH_3); ^1H NMR (CDCl_3 , minor product) δ 7.62–7.00 (m, 30 H, PPh₃), 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, $J_{\text{H-H}} = 7.1$ Hz, 3H, CH_2CH_3), 0.79 (s, 3H, Me); ^{13}C NMR (C_6D_6 , major product) δ 197.4 (t, $J_{\text{P-C}} = 19.3$ Hz, C_α), 140.6–123.9 (Ph), 118.4 (CN), 82.8 (Cp), 75.5 (CMeEt), 69.1 (CH), 29.8 (CH_2), 24.1 (CH_3), 8.5 (CH_3); ^{13}C NMR (C_6D_6 , minor product) δ 197.9 (t, $J_{\text{P-C}} = 19.6$ Hz, C_α), 140.6–123.9 (Ph), 117.9 (CN), 82.6 (Cp), 75.1 (CMeEt), 70.2 (CH), 26.8 (CH_2), 23.8 (CH_3), 9.1 (CH_3); ^{31}P NMR (C_6D_6) δ 52.6, 49.7 (AB, $J_{\text{P-P}} = 34.1$ Hz), 52.3, 49.7 (AB, $J_{\text{P-P}} = 34.3$ Hz) (5:4); MS (FAB, m/z) 829.2 ($\text{M}^+ + 1$), 567.3 ($\text{M}^+ + 1 - \text{PPh}_3$), 429.0 ($\text{M}^+ - \text{PPh}_3$, CNCHCN- $(\text{CH}_3)_2\text{CH}_2\text{CH}_3\text{O}$). Anal. Calcd for $\text{C}_{48}\text{H}_{44}\text{N}_2\text{OP}_2\text{Ru}$: 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*-Bu₄NOH (0.5 mL) in 20 mL of CH_2Cl_2 at room temperature. A mixture containing two diastereomers in a 5:1 ratio was isolated. Spectroscopic data for **5c**: ^1H NMR (CDCl_3 , major isomer) δ 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, $J_{\text{H-H}} = 11.4$ Hz, CH); ^1H NMR (CDCl_3 , minor isomer) δ 7.62–6.80 (m, 35 H, Ph), 4.57 (d, 1H, $J_{\text{H-H}} = 11.4$ Hz, OCH), 4.41 (s, 5H, Cp), 4.01 (d, 1H, $J_{\text{H-H}} = 11.4$ Hz, CCH); ^{13}C NMR (C_6D_6 , major isomer) δ 197.5 (t, $J_{\text{P-C}} = 19.7$ Hz, C_α), 139.1–121.6 (Ph), 119.5 (CN), 86.4 (CHPh), 85.6 (Cp), 80.1 (CH); ^{13}C NMR (C_6D_6 , minor isomer) δ 196.4 (t, $J_{\text{P-C}} = 19.6$ Hz, C_α), 119.1 (CN), 85.3 (CHPh), 85.1 (Cp), 78.3 (CH); ^{31}P NMR (C_6D_6) δ 51.8, 49.4 (AB, $J_{\text{P-P}} = 34.5$ Hz), 51.2, 49.7 (AB, $J_{\text{P-P}} = 34.4$ Hz) (5:1); MS (FAB, m/z) 863.1 ($\text{M}^+ + 1$), 602.3 ($\text{M}^+ + 1 - \text{PPh}_3$), 429.0 ($\text{M}^+ - \text{PPh}_3$, CNCHCNPhHO). Anal. Calcd for $\text{C}_{51}\text{H}_{42}\text{N}_2\text{OP}_2\text{Ru}$: 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_2Cl_2 /ether (1:3) gave **5d** (0.19 g, 78% yield). Spectroscopic data for **5d**: ^1H NMR (CDCl_3) δ 7.62–6.94 (m, 30 H, PPh₃), 4.48 (s, 5H, Cp), 4.05 (d, 1H, $J_{\text{H-H}} = 9.3$ Hz, CHCN), 3.80 (d, 1H, $J_{\text{H-H}} = 9.3$ Hz, OCH), 0.94 (s, 9H, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (C_6D_6) δ 195.1 (t, $J_{\text{P-C}} = 19.4$ Hz, C_α), 139.4–122.8 (Ph), 118.1 (CN), 81.7 (Cp), 76.4 ($\text{CC}(\text{CH}_3)_3$), 70.3 (CH), 57.1 (CMe_3), 29.4 (CMe_3); ^{31}P NMR

(C₆D₆) δ 51.6, 49.6 (AB, $J_{P-P} = 34.2$ Hz); MS (FAB, m/z) 843.3 (M⁺ + 1), 581.1 (M⁺ + 1 - PPh₃), 429.0 (M⁺ - PPh₃, CNCHNCMe₃O). Anal. Calcd for C₄₉H₄₆N₂OP₂Ru: C, 69.90; H, 5.51; N, 3.33. Found: C, 70.00; H, 5.58; N, 3.39.

Synthesis of 5e. To 50 mL of a CH₂Cl₂ solution of **2a** (0.07 g, 0.084 mmol) were added a slight excess of ferrocenecarboxaldehyde (0.02 g, 0.12 mmol) and *n*-Bu₄NOH (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**: ¹H NMR (C₆D₆) δ 7.56–7.01 (m, 30 H, Ph), 5.09 (d, 1H, $J_{H-H} = 9.4$ Hz, OCH), 4.47 (s, 5H, Cp), 4.21 (d, 1H, $J_{H-H} = 9.4$ Hz, NCH), 4.07 (br, 2H, Fe(C₅H₄)CO), 4.05 (br, 2H, Fe(C₅H₄)CO), 3.94 (s, 5H, (C₅H₅)Fe); ¹³C NMR (C₆D₆) δ 197.5 (t, $J_{P-C} = 19.7$ Hz, C_o), 139.1–121.6 (m, Ph), 119.5 (CN), 99.1 (CHFe(C₅H₅)₂), 85.6 (Cp), 80.7 (CHCN), 71.4 (C₅H₅), 68.6 (C₅H₅), 64.6 (C₅H₅), 64.1 (C₅H₅); ³¹P NMR (CDCl₃) δ 51.3, 50.8 (AB, $J_{P-P} = 34.9$ Hz); MS (FAB, m/z) 971.3 (M⁺ + 1), 709.2 (M⁺ + 1 - PPh₃), 429.0 (M⁺ - PPh₃, CNCHNC Fe(C₅H₅)₂O). Anal. Calcd for C₅₅H₄₆N₂OP₂RuFe: 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*-Bu₄NOH (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 for **6a**: ¹H NMR (C₆D₆) δ 7.55–6.97 (m, 30 H, PPh₃), 5.69 (ddd, $J_{H-H} = 16.9, 9.9, 7.1$ Hz, 1H, HC=), 5.23 (dd, $J_{H-H} = 16.9, 2.4$ Hz, 1H, =CHH), 5.01 (dd, $J_{H-H} = 9.9, 2.4$ 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); ¹³C NMR (C₆D₆) δ 198.4 (t, $J_{P-C} = 18.1$ Hz, C_o), 152.4 (CH=CH₂), 142.3–123.6 (Ph), 110.4 (CH=CH₂), 83.7 (Cp), 78.4 (CMe₂), 64.1 (CH), 28.5 (CH₃), 24.2 (CH₃); ³¹P NMR (CDCl₃) δ 51.2, 50.4 (AB, $J_{P-P} = 34.7$ Hz); MS (FAB, m/z) 816.3 (M⁺ + 1), 554.1 (M⁺ + 1 - PPh₃), 429.0 (M⁺ - PPh₃, CNCH(HC=CH₂)C(CH₃)₂O). Anal. Calcd for C₄₈H₄₅NOP₂Ru: 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*-Bu₄NOH (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 (C₆D₆) δ 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); ¹³C NMR (C₆D₆) δ 187.3 (t, $J_{P-C} = 19.4$ Hz, C_o), 143.6–126.9 (Ph), 87.5 (Cp), 85.9 (CH), 79.8 (CMe₂), 28.3 (CH₃), 27.9 (CH₃); ³¹P NMR (C₆D₆) δ 51.8, 50.1 (AB, $J_{P-P} = 34.6$ Hz); MS (FAB) m/z : 866.3 (M⁺ + 1), 604.1 (M⁺ + 1 - PPh₃), 429.0 (M⁺ + 1 - PPh₃, CNCHPhCMe₂O). Anal. Calcd for C₅₂H₄₇NOP₂Ru: C, 72.41; H, 5.38; N, 1.60. Found: C, 72.19; H, 5.53; N, 1.69.

Synthesis of 7a*. To a solution of **2c*** (0.25 g, 0.30 mmol) in 20 mL of acetone was added a solution of *n*-Bu₄NOH (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***. Complex **7a*** was recrystallized from *n*-hexane (0.15 g, 60% yield). Spectroscopic data for **7a***: IR (KBr) 1633 cm⁻¹ (m, $\nu_{C=N}$); ¹H NMR (C₆D₆) δ 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, CH₃), 1.50 (s, 15H, 5CH₃), 0.82 (s, 3H, CH₃); ¹³C NMR (C₆D₆) δ 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, CMe₂), 25.2 (s, Me₂), 24.8 (m, dppp), 10.5 (s, 5Me); ³¹P NMR (C₆D₆) δ 52.94, 45.35 (2 d, $J_{P-P} = 51.1$ Hz); MS (FAB, m/z , Ru¹⁰²): 824.2 (M⁺), 766.2 (M⁺ - CO(CH₃)₂). Anal. Calcd for C₄₈H₅₃NOP₂Ru: 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 CH₂Cl₂ at room temperature. Spectroscopic data for **7b**: ¹H NMR (C₆D₆, major isomer) δ 7.58–6.94 (m, 40 H, Ph), 5.12 (d, 1H, $J_{H-H} = 11.4$ Hz, NCHPh), 4.64 (s, 5H, Cp), 4.49 (d, 1H, $J_{H-H} = 11.4$ Hz, OCHPh); ¹H NMR (C₆D₆, minor isomer) δ 7.58–6.94 (m, 40 H, Ph), 5.12 (d, 1H, $J_{H-H} = 11.4$ Hz, OCHPh), 4.73 (s, 5H, Cp), 4.49 (d, 1H, $J_{H-H} = 11.4$ Hz, NCHPh); ³¹P NMR (C₆D₆) δ 51.8, 49.3 (AB, $J_{P-P} = 34.7$ Hz), 51.0, 49.7 (AB, $J_{P-P} = 34.6$ Hz) (4:1); MS (FAB, m/z) 914.2 (M⁺ + 1), 651.2 (M⁺ + 1 - PPh₃), 429.0 (M⁺ - PPh₃, CNCHPhCPhHO). Anal. Calcd for C₅₆H₄₇NOP₂Ru: 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 CH₂Cl₂ at room temperature. Spectroscopic data for **7c**: ¹H NMR (C₆D₆, major) δ 7.57–6.99 (m, 35H, Ph), 4.85 (s, 1H, CH), 4.63 (s, 5H, Cp), 1.78 (m, 1H, CH₂), 1.58 (m, 1H, CH₂), 1.24 (s, 3H, Me), 0.87 (m, 3H, CH₃); ¹H NMR (C₆D₆, minor) δ 7.57–6.99 (m, 35 H, Ph), 4.76 (s, 1H, CH), 4.61 (s, 5H, Cp), 1.78 (m, 1H, CH₂), 1.58 (m, 1H, CH₂), 0.96 (t, $J_{H-H} = 7.3$ Hz, 3H, CH₂CH₃), 0.64 (s, 3H, Me); ³¹P NMR (C₆D₆) δ 52.1, 49.6 (AB, $J_{P-P} = 34.7$ Hz), 52.2, 49.6 (AB, $J_{P-P} = 34.6$ Hz) (5:4); MS (FAB, m/z) 880.3 (M⁺ + 1), 618.2 (M⁺ + 1 - PPh₃), 429.0 (M⁺ - PPh₃, CNCHPhCMe(Et)O). Anal. Calcd for C₅₅H₄₉NOP₂Ru: 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 CH₂Cl₂/hexane (1:5) gave **7d** (0.46 g, 87% yield). Spectroscopic data for **7d**: ¹H NMR (C₆D₆) δ 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); ³¹P NMR (C₆D₆) δ 52.0, 48.9 (AB, $J_{P-P} = 34.7$ Hz); MS (FAB, m/z) 894.3 (M⁺ + 1), 632.2 (M⁺ + 1 - PPh₃), 429.0 (M⁺ - PPh₃, CNCHPhCHC(Me)₃O). Anal. Calcd for C₅₄H₅₁NOP₂Ru: 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 CH₂Cl₂ solution of **2c** (0.47 g, 0.53 mmol) were added excess ferrocenecarboxaldehyde (0.14 g, 0.67 mmol) and *n*-Bu₄NOH (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**: ¹H NMR (C₆D₆) δ 7.52–6.98 (m, 35 H, Ph), 5.06 (d, 1H, $J_{H-H} = 9.5$ Hz, NCHPh), 4.64 (s, 5H, Cp), 4.53 (d, 1H, $J_{H-H} = 9.5$ Hz, OCH), 4.04 (br, 2H, Fe(C₅H₄)CO), 3.97 (br, 2H, Fe(C₅H₄)CO), 3.91 (s, 5H, (C₅H₅)Fe); ³¹P NMR (C₆D₆) δ 51.0, 50.7 (AB, $J_{P-P} = 35.1$ Hz); MS (FAB, m/z) 1021.1 (M⁺ + 1), 759.2 (M⁺ + 1 - PPh₃), 429.0 (M⁺ - PPh₃, CNCHPhCH₂Fe(C₅H₅)₂O). Anal. Calcd for C₆₀H₅₁NOP₂RuFe: 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 CH₂Cl₂/hexane (1:5) gave **7f** (0.23 g, 77% yield). Spectroscopic data for **7f**: ¹H NMR (C₆D₆) δ 7.33–6.08 (m, 40 H, Ph), 5.02 (s, 1H, CH), 4.83 (s, 5H, Cp), 3.66 (s, 3H, Me); ³¹P NMR (C₆D₆) δ 52.3, 48.9 (AB, $J_{P-P} = 34.4$ Hz); ¹³C NMR (C₆D₆)

δ 191.3 (t, $J_{P-C} = 19.1$ Hz, C_{α}), 141.2–127.3 (Ph), 88.7 (Cp), 84.7 (CHPh), 81.2 (CPh(OMe)), 56.9 (CH_3); MS (FAB, m/z) 944.3 ($M^+ + 1$), 682.1 ($M^+ + 1 - PPh_3$), 429.0 ($M^+ - PPh_3$, 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_2Cl_2 /hexane (1:5) gave **7g** (0.17 g, 54% yield). Spectroscopic data for **7g**: 1H NMR (C_6D_6) δ 7.49–7.31 (m, 35 H, Ph), 5.12 (s, 1H, CH), 4.77 (s, 5H, Cp), 2.46 (s, 6H, NMe_2), 1.13 (s, 3H, Me); ^{31}P NMR (C_6D_6) δ 51.8.0, 49.8 (AB, $J_{P-P} = 34.6$ Hz); ^{13}C NMR (C_6D_6) δ 192.7 (t, $J_{P-C} = 19.4$ Hz, C_{α}), 137.9–126.5 (m, Ph), 89.1 (Cp), 86.9 (CHPh), 82.0 (CMe), 37.6 ($N(CH_3)_2$), 24.3 (CH_3); MS (FAB, m/z) 894.2 ($M^+ + 1$), 632.1 ($M^+ + 1 - PPh_3$), 429.0 ($M^+ - PPh_3$, CNCHPhCMe(NMe_2)O).

Synthesis of $\{[Ru]CNCHPhC(CH_3)_2OH\}[PF_6]$ (8a***).** A solution of **2c*** (0.22 g, 0.26 mmol), NaOMe (0.25 g, 4.5 mmol), and KPF_6 (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^{-1} (s, ν_{CN}), 3576 cm^{-1} (br, ν_{OH}); 1H NMR ($CDCl_3$) δ 7.53–7.12 (m, 30H, Ph), 5.46 (s, 1H, CH), 2.67–2.27 (m, 6H, $CH_2CH_2CH_2$), 2.53 (s, 1H, OH), 1.39 (s, 15H, $5CH_3$), 1.26 (s, 3H, CH_3), 1.27 (s, 3H, CH_3); ^{31}P NMR ($CDCl_3$) δ 38.44, 38.06 (AB, $J_{P-P} = 46.5$ Hz); MS (FAB, m/z , Ru^{102}) 824.3 (M^+), 766.3 ($M^+ - CMe_2OH$). Anal. Calcd for $C_{48}H_{54}F_6NOP_3Ru$: C, 59.50; H, 5.58; N, 1.44. Found: C, 59.59; H, 5.44; N, 1.51.

Reduction of 7a by $NaBH_3CN$ in MeOH. To a solution of **7a** (1.20 g, 1.38 mmol) in 30 mL of MeOH at room temperature was added $NaBH_3CN$ (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 $PhCH_2-CMe_2OH$ (**10a**; 0.21 g, 96% yield). Spectroscopic data for **10a**: 1H NMR (C_6D_6) δ 7.24–7.04 (m, 5 H, Ph), 2.56 (s, 2H, CH_2), 1.24 (s, 1H, OH), 1.04 (s, 6H, 2Me); ^{13}C NMR (C_6D_6) δ 138.5,

130.8, 128.3, 126.5 (Ph), 70.3 (COH), 50.0 (CMe), 29.3 (CH_3); high-resolution MS (m/z) found 150.1041, calcd 150.2200. Anal. Calcd for $C_{10}H_{14}O$: 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 $0.30 \times 0.25 \times 0.20$ mm³ 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. SADABS³⁴ (Siemens area detector absorption) correction was applied, and decay was negligible. Data were processed, and the structures were solved and refined by the SHELXTL³⁵ program. The structure was solved using direct methods and confirmed by Patterson methods refining on F^2 using all data.³⁶ 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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(34) SAINT (Siemens Area Detector Integration) program; Siemens Analytical X-ray, Madison, WI, 1995.

(35) (a) The SADABS 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.

(36) 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 $P = [(max; 0, F_o^2) + 2F_c^2]/3$.