Cyclization Reactions of Ruthenium Vinylidene Complexes

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Treatment of [Ru]−C═C(Ph)C(═NPh)S (**2**, [Ru] = (η^5-C_5H_5)(dppe)Ru, dppe = Ph_2PCH_2-CH_2PPh_2) with ICH_2CN at room temperature affords the S-alkylation product [Ru]═C═C(Ph)C(═NPh)SCH_2R^+ (**3a**, R = CN). Deprotonation of **3a** by *n*-Bu_4NOH in acetone induces a novel cyclization reaction and yields the neutral five-membered-ring heterocyclic complex [Ru]−C═C(Ph)C(═NPh)SCHCN (**5a**), which isomerizes to the 2-aminothiophene complex [Ru]−C═C(CN)SC(NHPh)═C(Ph) (**6a**). Treatment of **2** with organic bromides $BrCH_2R$ affords both S-alkylation products (**3b**, R = CO_2CH_3; **3c**, R = *p*-C_6H_4CN; **3d**, R = Ph) and N-alkylation products [Ru]═C═C(Ph)C(═S)NPhCH_2R^+ (**4b**, R = CO_2CH_3; **4c**, R = *p*-C_6H_4CN; **4d**, R = Ph) in varying ratios. Base-induced cyclization of a mixture of **3b** and **4b** occurs only for the **3b** component to afford [Ru]−C═C(Ph)C(═NPh)S$CHCO_2CH_3$ (**5b**), whereas cyclization of a mixture of **3c** and **4c** occurs for both complexes, yielding **5c** and the pyrrole-2-thione complex [Ru]−C═C(Ph)C(═S)N(Ph)CH(*p*-C_6H_4CN) (**7c**), respectively. Cyclization of a **3d**−**4d** mixture occurs only for **4d** to afford [Ru]−C═C(Ph)C(═S)NPhCHPh (**7d**). The structures of **6a** and **7c** were determined by single-crystal X-ray diffraction analysis.

Introduction

Metal acetylide complexes has been the focus of many recent studies because of their applications in organometallic[1−4] and materials[5−8] chemistry. A common reaction of a metal acetylide is a [2 + 2] cycloaddition of the triple bond with unsaturated organic substrates,[9] such as CS_2,[10−12] $(NC)_2C═C(CF_3)_2$, and $(NC)_2C═C(CN)_2$.[13−15] Recently we reported[16] a similar cycloaddition reaction of the ruthenium acetylide complex {Ru}C≡CPh (**1′,** {Ru} = (η^5-C_5H_5)(PPh_3)[$P(OMe)_3$]Ru) with isothiocyanates RNCS to afford {Ru}C═C(Ph)C(═NR)S (**2′**). This cycloaddition was found to be reversible, and in the absence of free isothiocyanate, the acetylide complex was gradually regenerated. However, in the presence of excess isothiocyanate, the six-membered-ring complex {Ru}C═C(Ph)C(═S)N(R)C(═NR)S, containing two isothiocyanate molecules, was obtained. This indicates that the reversed cycloaddition is a stepwise process. Formation of the six-membered-ring complex was thus rationalized by opening of the four-membered ring of **2′** via cleavage of the C_α−S bond, followed by coupling of a second isothiocyanate molecule. Opening of the four-membered ring of **2′** could provide a zwitterionic complex with the negative charge localized at one of the heteroatoms (S and N), and a subsequent alkylation reaction at the heteroatom site could be a useful reaction. We therefore reacted alkyl halides with the dppe analogue of the four-membered-ring complex. Herein we report that these alkylation reactions yield a number of vinylidene complexes.[17−21] Subsequent deprotonation-induced-cyclization reactions of these vinylidene complexes form neutral heterocyclopentenyl complexes.[4,22]

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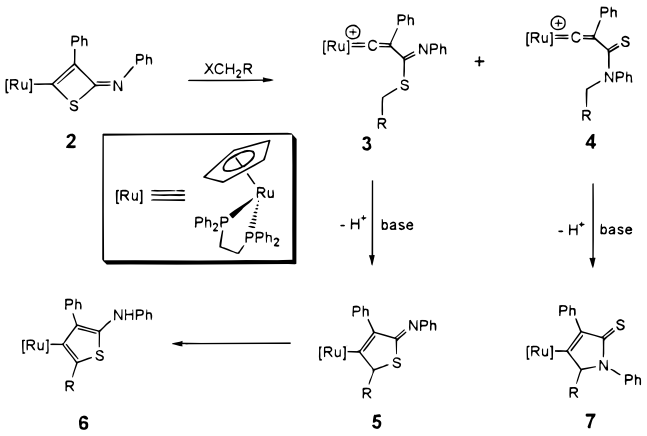
Scheme 1



Results and Discussion

Synthesis of Vinylidene Complexes. Treatment of [Ru]C≡CPh (**1**, [Ru] = (η^5-C_5H_5)(dppe)Ru, dppe = $Ph_2PCH_2CH_2PPh_2$) with PhNCS in CH_2Cl_2 at room temperature for 3 days affords the yellow [2 + 2] cycloaddition product [Ru]-C=C(Ph)C(=NPh)S (**2**).[23−26] On the basis of the chemical reactivity of the bis(triphenylphosphine) analogue of **2**,[16] we believe that **2** exists in two forms: a four-membered-ring structure and a zwitterionic structure formed by cleavage of the C_α−S bond of the four-membered ring. In the zwitterionic form the negative charge could be localized either at the S atom or at the N atom, thus rendering these atoms nucleophilic. Indeed, treatment of **2** with ICH_2CN affords the air-stable cationic vinylidene complex {[Ru]=C=C(Ph)C(=NPh)SCH_2CN}[I] (**3a**) in 87% yield. The alkylation is found to take place only at the S atom. The vinylidene ligand of **3a** was confirmed by the presence of a triplet ^{13}C resonance at δ 340.7 with J_{C-P} = 13.4 Hz assignable to C_α. The ^{31}P resonance of **3a** appears as a singlet at δ 78.1 due to the fluxional behavior of the vinylidene ligand. Interestingly, unlike other orange-red ruthenium vinylidene complexes, **3a** is purple.

Treatment of complex **2** with $BrCH_2CO_2CH_3$ in CH_2Cl_2 affords a mixture of two cationic vinylidene complexes, the S-alkylation product [Ru]=C=C(Ph)C(=NPh)$SCH_2CO_2CH_3^+$ (**3b**) and the N-alkylation product [Ru]=C=C(Ph)C(=S)N(Ph)$CH_2CO_2CH_3^+$ (**4b**) (Scheme 1), in a ratio of 3:2 and with a total yield of 78%. The ratio of **3b** to **4b** depends on the reaction temperature, with **3b** favored at lower temperature. Under reflux conditions, the **3b**:**4b** ratio was found to be ca. 1:1. Complexes **3b** and **4b** do not interconvert in solution and could not be separated by chromatography. The ^{31}P NMR spectrum of the mixture displays two singlet resonances at δ 77.2 and 79.0 attributed to **3b** and **4b**, respectively. In the ^1H NMR spectrum two resonances at δ 5.52 and 5.48 are assigned to the Cp groups of **3b** and **4b**, and resonances at δ 3.45 and 3.43 are assigned to the CH_2 groups of **3b** and **4b**, respectively. In the ^{13}C NMR spectrum of the mixture, two triplet resonances at δ 341.5 (J_{C-P} = 18.2 Hz) and 342.2 (J_{C-P} = 17.7 Hz) are assigned to Cα's of **3b** and **4b**, respectively, indicating that both are vinylidene complexes.

Other vinylidene complexes [Ru]=C=C(Ph)C(=NPh)-SCH_2R^+ (**3c**, R = *p*-C_6H_4CN; **3d**, R = Ph) and [Ru]=C=C(Ph)C(=S)N(Ph)CH_2R^+ (**4c**, R = *p*-C_6H_4CN; **4d**, R = Ph) were similarly prepared as mixtures at room temperature (**3c**:**4c** = 1:2, total yield 87%; **3d**:**4d** = 6:5, total yield 83%) by reacting **2** with organic bromides (Scheme 1). Alkylation reactions take place both at the N and the S atoms. Like **3a** and **3b**, complexes **3c**, **4c**, **3d**, and **4d** are all purple, air stable and thermally stable, soluble in polar solvents such as $CHCl_3$, CH_2Cl_2, acetone, and THF, and insoluble in ether and hexane. Generally complexes **3** and **4** are not separable by column chromatography. However, as described below, pure complexes can be obtained indirectly.

Deprotonation-Induced Cyclization of Vinylidene Complex 3a. Treatment of **3a** with *n*-Bu_4NOH (1M in MeOH) causes deprotonation of the methylene group, followed by a cyclization reaction affording the neutral complex [Ru]−C=C(Ph)C(=NPh)SCHCN (**5a**) (Scheme 1). Protonation of **5a** in $CHCl_3$ with CF_3COOH immediately gives **3a** in quantitative yield. In our attempt to purify **5a** by column chromatography, isomerization to the 2-aminothiophene complex [Ru]−C=C(CN)SC(NHPh)=CPh (**6a**) takes place. This conversion also occurs in benzene at room temperature in 3 h. No reaction was observed between complex **6a** and electrophiles such as CH_3I, ICH_2CN, and CH_3COOH. The transformation of **5a** to **6a** possibly proceeds via a hydrogen shift process. When the reaction is carried out at an appropriate concentration, single crystals of **6a** suitable for X-ray diffraction analysis can be obtained directly. The ^{31}P NMR spectrum of **5a** shows two doublet resonances at δ 72.30 and 69.12 with J_{P-P} = 29.76 Hz due to the presence of an asymmetric carbon center in the five-membered ring. The ^{31}P NMR spectrum of **6a** displays a broad resonance at δ 67.55 at room temperature which resolves into two doublets at δ 71.76 and 60.78 with J_{P-P} = 32.6 Hz at −80 °C, possibly due to the hindered flipping of the pyramidal nitrogen atom.

The structure of **6a** has been confirmed by a single-crystal X-ray diffraction study. An ORTEP diagram is shown in Figure 1, and selected bond distances and bond angles are given in Table 1. This complex adopts a distorted three-legged piano-stool geometry with the P1−Ru−P2, P1−Ru−C1, and P2−Ru−C1 angles being 83.30(3), 116.96(11), and 99.26(9)°, respectively. The metal center is coordinated to an sp^2 C4 carbon of the substituted 2-aminothiophene ligand. The Ru−C1 distance of 2.112(3) Å is typical for a Ru−C single bond, and the C1−C2 distance of 1.445(5) Å is slightly longer than that of a C−C double bond. Two other C−C bonds (1.390(5) Å for C1−C4 and 1.387(5) Å for C2−C3) indicate double bonds. The Ru−C1−C2 angle is 129.7(2)°, and the Ru−C1−C4 angle is 121.0(2)°, close to that expected for C(sp^2) hybridization. The C3−N1 distance of 1.379(4) Å indicates a single bond. The bond distances C4−S1 and C3−S1 of 1.755(4) and 1.724(4) Å, respec-

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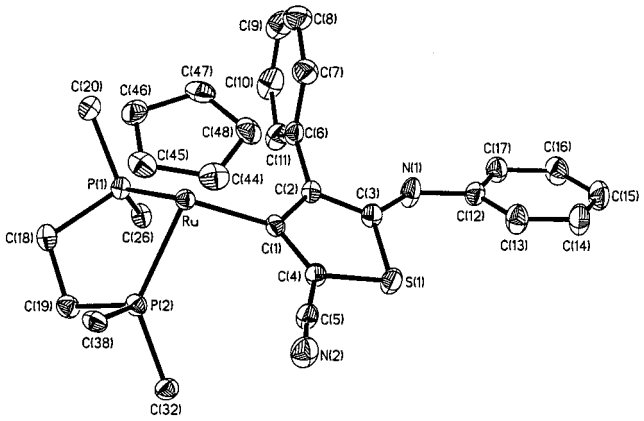

Figure 1. ORTEP drawing of **6a** with thermal ellipsoids shown at the 30% probability level. For the dppe phenyl groups, only the ipso carbons are shown.

Table 1. Selected Bond Distances (Å) and Angles (deg) for Cp(dppe)Ru−C(=C(CN)SC(NHPh)=CPh (6a)

Ru−C1	2.112(3)	C1−C2	1.445(5)
Ru−P1	2.2747(10)	C1−C4	1.390(5)
Ru−P2	2.3103(9)	C2−C3	1.387(4)
S1−C1	1.724(4)	C4−C5	1.412(5)
S1−C4	1.755(4)	N1−C12	1.402(5)
N1−C3	1.379(4)	N2−C5	1.153(5)
P1−Ru−P2	83.30(3)	C4−S1−C3	89.9(2)
P1−Ru−C1	116.96(11)	S1−C3−C2	112.2(3)
P2−Ru−C1	99.26(9)	C1−C2−C3	114.8(3)
Ru−C1−C4	121.0(2)	C2−C3−N1	124.5(3)
Ru−C1−C2	129.7(2)	S1−C3−N1	123.3(3)
C2−C1−C4	108.0(3)	C3−N1−C12	131.8(3)
C1−C4−S1	115.0(3)	C4−C5−N2	175.6(4)
C3−C2−C6	115.7(3)	C1−C4−C5	129.3(3)
C5−C4−S1	115.2(3)		

tively, are typical of a C−S single bond.[27] The C2−C3−S1 angle is 112.2(3)°, and the C1−C4−S1 angle is 115.0(3)°. The C3−S1−C4 angle of 89.9(2)° is smaller than that of a typical acyclic C−S−C angle.

Deprotonation-Induced Cyclization of Vinylidene Complexes 3b, 3c, and 4c. Treatment of a mixture of **3b** and **4b** in CH_2Cl_2 with NaOMe causes a color change from purple to orange-yellow. The ^{31}P NMR spectrum of the orange-yellow solution displays two doublet resonances at δ 73.4 and 64.5 with $J_{P-P} = 28.8$ Hz and a singlet resonance at δ 94.0. The former set is attributed to [Ru]−C(=C(Ph)C(=NPh)SCH(CO_2CH_3) (**5b**) and the latter to complex **2**. The ratio of **5b** to **2** is the same as that of **3b** to **4b**, indicating that formations of **5b** and **2** are derived from **3b** and **4b**, respectively. Under the reaction conditions, the organic portion ($CH_2CO_2CH_3$) of **4b** was removed to give **2**. Complexes **5b** and **2** were separated by column chromatography; **5b** decomposes at room temperature in 2 days in CH_2Cl_2. Treatment of a mixture of **3b** and **4b** with DBU (1,8-diazabicyclo[5,4,0]undecene) or *n*-Bu_4NOH also yielded a mixture of **5b** and **2**. Isomerization of **5b** to the 2-aminothiophene complex **6b** occurs in solution. As with **6a**, complex **6b** has a broad ^{31}P resonance at δ 65.10 at room temperature that at −40 °C resolves into two doubletsat δ 69.73 and 58.66 with $J_{P-P} = 32.2$ Hz.

When the mixture of **3c** and **4c** was treated with *n*-Bu_4NOH, an immediate color change from purple to yellow was observed. Interestingly, the deprotonation-induced cyclization occurred for both **3c** and **4c**, giving [Ru]−C(=C(Ph)C(=NPh)SCH(*p*-C_6H_4CN) (**5c**) and [Ru]-C(=C(*p*-C_6H_4CN)SC(NHPh)=CPh (**7c**), respectively. The ^{31}P NMR spectrum of the reaction mixture displays two pairs of doublet resonances: one appears at δ 69.31 and 67.54 with $J_{P-P} = 30.9$ Hz, assignable to **5c**, and the other at δ 94.88 and 91.79 with $J_{P-P} = 18.3$ Hz, assignable to **7c**. Both patterns arise from the asymmetric five-membered ring in **5c** and **7c**. These two complexes could be separated by chromatography using an alumina column. The ^1H NMR spectrum of **5c** shows resonances at δ 3.77 and 3.58 assignable to Cp and CH groups, respectively. Complex **5c** is stable at −20 °C but transforms to the corresponding 2-aminothiophene complex **6c** in solution at room temperature in 3 days. Heating a solution of **5c** accelerates this conversion. The ^{31}P NMR spectrum of **6c** displays an AX pattern at δ 72.15 and 66.40 with $J_{P-P} = 28.8$ Hz. In the ^1H NMR spectrum of **6c,** the Cp resonance appears at δ 3.47 and the NH resonance at δ 5.84. Protonation of **5c** with excess CF_3COOH yielded **3c**.

Deprotonation-Induced Cyclization of Vinylidene Complex 4d. Treatment of a mixture of **3d** and **4d** with NaOMe affords directly [Ru]−C(=C(Ph)C(=S)N(Ph)CH-Ph (**7d**), with no reaction occurring between **3d** and NaOMe. Complex **7d** is unstable and can be separated from **3d** by extraction with hexane. Complex **7d** was also obtained by treatment of the mixture of **3d** and **4d** with *n*-Bu_4NOH.

Facile deprotonation shows the acidic nature of the methylene protons of **3a**−**c**, which may be ascribed predominantly to the cationic character of the vinylidene complexes. It is not known why **3d** will not undergo deprotonation. Generally deprotonation of **4c** and **4d** is faster than that of **3**. The resulting complexes **7c** and **7d** are yellowish solids and are soluble in CH_2Cl_2, acetone, benzene, and ether. Complex **7c** is stable in acetone and in $CHCl_3$ for 7 days, while **7d** is relatively less stable in solution and decomposes in $CHCl_3$ in 8 h at room temperature. Both **7c** and **7d** react with acids such as CH_3COOH and CF_3COOH to give **4c** and **4d**, respectively. The spectroscopic data of both complexes are similar.

The molecular structure of **7c** has been confirmed by a single-crystal X-ray diffraction study. An ORTEP diagram is shown in Figure 2, and selected bond distances and bond angles are given in Table 2. The metal center is coordinated to the sp^2 carbon of the substituted pyrrole-2-thione ligand. The P1−Ru−P2, P1−Ru−C1, and P2−Ru−C1 angles are 83.75(4), 99.18-(9), and 99.40(9)°, respectively. The Ru−C1 distance of 2.094(3) Å is typical for a Ru−C single bond, and the C1−C2 distance of 1.368(4) Å indicates a C−C double bond.[27] Two other C−C bonds (1.522(4) Å for C1−C4 and 1.469(4) Å for C2−C3) are slightly different but are still within the range of a single bond, as are the two C−N bonds (1.479(4) Å for N1−C4 and 1.353(4) Å for N1−C3). Of the analogous bonds (C1−C4 vs C2−C3 and N1−C3 vs N1−C4) in the five-membered ring the one closer to the metal center is generally slightly longer.

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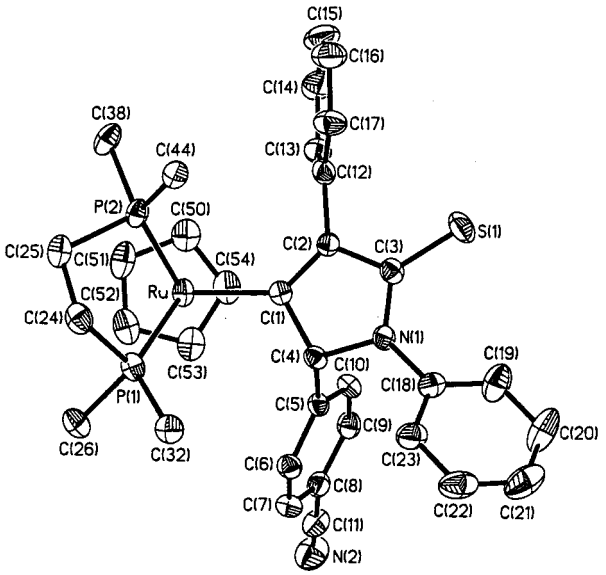

Figure 2. ORTEP drawing of **7c** with thermal ellipsoids shown at the 30% probability level. For the dppe phenyl groups, only the ipso carbons are shown.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Cp(dppe)Ru−C(=C(Ph)C(=S)N(Ph)CH(*p*-C_6H_4CN) (7c)

Ru−C1	2.094(3)	C1−C2	1.368(4)
Ru−P1	2.3249(10)	C1−C4	1.522(4)
Ru−P2	2.2840(10)	C2−C3	1.469(4)
S1−C3	1.664(3)	C4−C5	1.520(5)
N1−C4	1.479(4)	N1−C18	1.427(4)
N1−C3	1.379(4)	N2−C11	1.144(5)
P1−Ru−P2	83.75(4)	C4−N1−C3	109.9(3)
P1−Ru−C1	99.18(9)	S1−C3−C2	126.7(3)
P2−Ru−C1	99.40(9)	C1−C2−C12	130.2(3)
Ru−C1−C4	121.1(2)	C2−C3−S1	126.7(3)
Ru−C1−C2	132.8(2)	S1−C3−N1	125.6(3)
C2−C1−C4	105.7(3)	C3−N1−C18	127.8(3)
C1−C4−N1	105.0(2)	C5−C4−N1	110.4(3)
C3−C2−C1	111.4(3)	C1−C4−C5	114.0(3)
C2−C3−N1	107.8(3)		

This has also been observed in ruthenium cyclopropenyl complexes. The bond distance of 1.664(3) Å for C3−S1 is typical of a C−S double bond.[27]

Concluding Remarks. Alkylations of the ruthenium complex [Ru]−C(=C(Ph)C(=NPh)S with various organic halides XCH_2R take place at both S and N atoms, affording vinylidene complexes **3** and **4**, respectively. Deprotonation of these vinylidene complexes causes ring closure, yielding metal complexes containing heterocyclic ligands. Using this method, neutral 2-aminothiophene complexes [Ru]−C(=C(R)SC(NHPh)=CPh (**6a**, R = CN; **6b**, R = CO_2CH_3; **6c**, R = *p*-C_6H_4CN) and pyrrole-2-thione complexes [Ru]−C(=C(Ph)C(=S)N(Ph)CHR (**7c**, R = *p*-C_6H_4CN; **7d**, R = Ph) are all obtainable in moderate to high yield. We are currently investigating possible asymmetric induction by using the chiral ruthenium metal center with different phosphine ligands.

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 sodium diphenylketyl. All other solvents and reagents were of reagent grade and were used as received. NMR spectra were recorded on Bruker AC-200 and AM-300WB FT-NMR spectrometers at room temperature (unless states otherwise) and are reported in units of δ with residual protons in the solvents as a standard ($CDCl_3$, δ 7.24; C_2D_6O, δ 2.04). FAB mass spectra were recorded on a JEOL SX-102A spectrometer. The complexes [Ru]C≡CPh (**1**, [Ru] = (η^5-C_5H_5)(dppe)Ru, dppe = Ph_2PCH_2-CH_2PPh_2) and [Ru]−C(=C(Ph)C(=NPh)S (**2**) were prepared according to the methods reported in the literature.[16] Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument located at the National Taiwan University.

Synthesis of {[Ru]=C=C(Ph)S(=NPh)CH_2CN}[I] (3a). To a CH_2Cl_2 (20.0 mL) solution of **2** (200 mg, 0.250 mmol) was added ICH_2CN (0.10 mL, 0.75 mmol) under nitrogen. The resulting solution was stirred at room temperature for 2 h; then the solvent was reduced to 5 mL. This mixture was slowly added to 60 mL of vigorously stirred diethyl ether. The purple-red precipitate thus formed was filtered and washed with diethyl ether and hexane and dried under vacuum to give {[Ru]=C=C(Ph)C(=NPh)SCH_2CN}[I] (**3a**; 214.7 mg, 0.222 mmol) in 89% yield. Spectroscopic data for **3a**: ^{1}H NMR ($CDCl_3$) δ 7.63−6.32 (m, 30H, Ph), 5.44 (s, 5H, Cp), 3.53 (s, 2H, CH_2), 3.50−3.00 (m, 4H, CH_2); ^{31}P NMR ($CDCl_3$) δ 77.55; ^{13}C NMR ($CDCl_3$) δ 340.7 (t, C_α, J_{C-P} = 13.40 Hz), 148.6 (s, S*C*N), 132.7−120.6 (Ph and C_β), 117.9 (CN), 93.2 (Cp), 28.1 (t, PCH_2, J_{C-P} = 25.6 Hz), 17.4 (s, CH_2); MS (*m*/*z*, Ru^{102}) 841.1 (M^+ − I), 565.0 (M^+ − CCPh − PhNCS − CH_2CN). Anal. Calcd for $C_{48}H_{41}N_2P_2SRuI$ (967.80): C, 59.57; H, 4.27; N, 2.89. Found: C, 59.23; H, 4.58; N, 3.12.

Synthesis of {[Ru]=C=C(Ph)C(=NPh)S$CH_2CO_2CH_3$}-[Br] (3b) and {[Ru]=C=C(Ph)C(=S)N(Ph)$CH_2CO_2CH_3$}-[Br] (4b). To a CH_2Cl_2 solution (20 mL) of **2** (200 mg, 0.250 mmol) was added $BrCH_2CO_2CH_3$ (0.1 mL, 0.75 mmol). The resulting solution was stirred at room temperature for 3 h. ^{1}H and ^{31}P NMR spectra of the mixture indicated formation of the two major products **3b** and **4b**. Then the solvent was reduced to 5 mL. This mixture was slowly added to 60 mL of vigorously stirred diethyl ether. The purple-red precipitate was filtered off, washed with diethyl ether and hexane, and dried under vacuum to give a mixture of **3b** and **4b** (190.6 mg, 0.200 mmol) in a total yield of 80%. The ^{31}P NMR spectrum of the mixture displayed resonances attributed to **3b** and **4b** in a 3:2 ratio. Spectroscopic data for **3b**: ^{1}H NMR ($CDCl_3$) δ 7.58−6.76 (m, 30H, Ph), 5.52 (s, 5H, Cp), 3.68 (s, 3H, OCH_3), 3.45 (s, 2H, CH_2), 3.00−2.65 (m, 4H, PCH_2CH_2P); ^{31}P NMR ($CDCl_3$) δ 77.23; ^{13}C NMR ($CDCl_3$) δ 341.5 (t, C_α, J_{C-P} = 18.2 Hz), 169.5 (CO), 145.6 (SCN), 141.9−121.6 (Ph and C_β), 94.5 (Cp), 53.7 (OCH_3), 35.7 (CH_2), 28.4 (t, PCH_2, J_{C-P} = 23.2 Hz); MS (*m*/*z*, Ru^{102}) 874.1 (M^+ − Br), 565.0 (M^+ − CCPh − PhNCS − CH_2-CO_2CH_3). Spectroscopic data for **4b**: ^{1}H NMR ($CDCl_3$) 7.54−6.35 (m, 30H, Ph), 5.48 (s, 5H, Cp), 3.59 (s, 3H, OCH_3), 3.43 (s, 2H, CH_2), 2.80−2.35 (m, 4H, PCH_2CH_2P); ^{31}P NMR ($CDCl_3$) δ 79.02; ^{13}C NMR ($CDCl_3$) 342.2 (t, C_α, J_{C-P} = 17.7 Hz), 183.4 (CS), 168.1 (CO), 145.0−120.5 (Ph and C_β), 93.3 (Cp), 36.9 (CH_2), 30.3 (t, PCH_2, J_{C-P} = 22.1 Hz); MS (*m*/*z*, Ru^{102}) 847.1 (M^+ − Br), 565.0 (M^+ − CCPh-PhNCS − $CH_2CO_2CH_3$). Anal. Calcd for $C_{49}H_{44}NO_2P_2SRuBr$ (953.83): C, 61.70; H, 4.65; N, 1.47. Found for the mixture of **3b** and **4b**: C, 60.93; H, 4.55; N, 1.32.

Mixtures of the complexes {[Ru]=C=C(Ph)C(=NPh)SCH_2-(*p*-C_6H_4CN)}[Br] (**3c**) and {[Ru]=C=C(Ph)C(=S)N(Ph)CH_2(*p*-C_6H_4CN)}[Br] (**4c**) (**3c**:**4c** = 1:2, 87% total yield) as well as {[Ru]=C=C(Ph)C(=NPh)SCH_2Ph}[Br] (**3d**) and {[Ru]=C=C(Ph)-C(=S)N(Ph)CH_2Ph}[Br] (**4d**) (**3d**:**4d** = 6:5, 83% total yield) were prepared using the same procedure as that for **3b** and **4b**. Spectroscopic data for **3c**: ^{1}H NMR ($CDCl_3$) δ 7.60−

6.18 (m, 34H, Ph), 5.39 (s, 5H, Cp), 3.33 (s, 2H, CH_2), 3.20−2.60 (m, 4H, PCH_2CH_2P); ^{31}P NMR ($CDCl_3$) δ 77.98; ^{13}C NMR ($CDCl_3$) δ 354.7 (t, C_α, J_{C-P} = 12.1 Hz), 182.5 (s, S*C*N), 140.4−126.6 (Ph and C_β), 111.6 (CN), 93.6 (Cp), 30.9 (CH_2), 28.1 (t, PCH_2, J_{C-P} = 23.7 Hz); MS (*m*/*z*, Ru^{102}) 917.2 (M^+ − Br), 565.1 (M^+ − CCPh − PhNCS−$CH_2C_6H_4CN$). Spectroscopic data for **4c**: ^1H NMR ($CDCl_3$) δ 7.59−6.08 (m, 34H, Ph), 5.44 (s, 5H, Cp), 3.38 (s, 2H, CH_2), 3.40−2.80 (m, 4H, PCH_2CH_2P); ^{31}P NMR ($CDCl_3$) δ 79.51; ^{13}C NMR ($CDCl_3$): δ 354.0 (t, C_α, J_{C-P} = 15.2 Hz), 218.2 (s, CS), 135.8−126.4 (Ph and C_β), 92.5 (Cp), 31.4 (CH_2), 27.7 (t, PCH_2, J_{C-P} = 23.2 Hz); MS (*m*/*z*, Ru^{102}) 917.2 (M^+ − Br), 565.1 (M^+ − CCPh − PhNCS − $CH_2C_6H_4$-CN). Anal. Calcd for $C_{54}H_{45}N_2P_2SRuBr$ (996.89): C, 65.06; H, 4.55; N, 2.81. Found for the mixture of **3c** and **4c**: C, 64.92; H, 4.46; N, 2.72. Spectroscopic data for **3d**: ^1H NMR ($CDCl_3$) δ 7.75−6.25 (m, 35H, Ph), 5.40 (s, 5H, Cp), 4.46 (s, 2H, CH_2), 3.10−3.40 (m, 4H, PCH_2CH_2P); ^{31}P NMR ($CDCl_3$) δ 78.12; ^{13}C NMR ($CDCl_3$) δ 184.0 (s, S*C*N), 145.3−121.2 (Ph and C_β), 93.7 (Cp), 28.9 (t, PCH_2, J_{C-P} = 21.9 Hz), 15.9 (CH_2); MS (*m*/*z*, Ru^{102}) 892.3 (M^+ − Br), 565.1 (M^+ − CCPh − PhNCS − $CH_2C_6H_5$). Spectroscopic data for **4d**: ^1H NMR ($CDCl_3$) δ 7.59−6.06 (m, 35H, Ph), 5.33 (s, 5H, Cp), 3.30 (s, 2H, CH_2), 3.10−3.40 (m, 4H, PCH_2CH_2P); ^{31}P NMR ($CDCl_3$) δ 81.11; ^{13}C NMR ($CDCl_3$) δ 207.4 (s, CS), 143.1−120.3 (Ph and C_β), 92.8 (Cp), 29.2 (t, PCH_2, J_{C-P} = 23.4 Hz), 14.7 (CH_2); MS (*m*/*z*, Ru^{102}) 892.3 (M^+ − Br), 565.1 (M^+ − CCPh − PhNCS − $CH_2C_6H_5$). Anal. Calcd for $C_{53}H_{46}NP_2SRuBr$ (971.88): C, 65.49; H, 4.77; N, 1.44. Found for the mixture of **3d** and **4d**: C, 65.74; H, 4.75; N, 1.51.

Synthesis of [Ru]−C═C(CN)SC(NHPh)═CPh (6a). To a solution of **3a** (300 mg, 0.310 mmol) in 15 mL of acetone was added *n*-Bu_4NOH (1 mL, 1 M in MeOH). The mixture was stirred at room temperature for 30 min to give a bright yellow solution, and then the solvent was reduced to 3.0 mL. The residue was chromatographed on a alumina column. The yellow product was eluted with benzene. The solvent of the eluate was reduced to ca. 1 mL, and 15 mL of hexane was added to give yellow precipitates. The solid product was filtered and washed with 10 mL of hexane to give [Ru]−C═C(CN)SC(NHPh)═CPh (**6a**; 177.0 mg, 0.211 mmol) in 68% yield. Spectroscopic data for **6a**: ^1H NMR ($CDCl_3$) δ 7.34−6.41 (m, 30H, Ph), 5.47 (s, NH), 3.92 (s, 5H, Cp), 2.13, 1.68 (2m, 4H, CH_2); ^{31}P NMR ($CDCl_3$) δ 67.55 (br); ^{31}P NMR (acetone at −80 °C) δ 71.76, 60.79 (2d, J_{P-P} = 32.6 Hz); ^{13}C NMR ($CDCl_3$) δ 171.8 (s, S*C*N), 141.5−120.8 (Ph and C_α, C_β), 116.1 (CN), 84.2 (Cp), 33.7, 33.3 (2t, PCH2, J_{C-P} = 22.6 Hz); MS (*m*/*z*, Ru^{102}) 840.0 (M^+), 565.0 (M^+ − CCPh − PhNCS − CHCN). Anal. Calcd for $C_{48}H_{40}N_2P_2SRu$ (839.89): C, 68.64; H, 4.80; N, 3.34. Found: C, 69.02; H, 4.58; N, 3.27. The intermediate [Ru]−C═C(Ph)S(═NPh)CHCN (**5a**) was observed in about 10 min when the reaction was monitored by NMR spectroscopy. Complex **5a** is unstable and readily converted to **6a** when passed through an alumina column at room temperature. Spectroscopic data for **5a**: ^1H NMR ($CDCl_3$) δ 7.81−6.28 (m, 30H, Ph), 4.65 (s, H, CHCN), 4.17 (s, 5H, Cp), 2.32, 2.08 (2m, 4H, CH_2); ^{31}P NMR ($CDCl_3$) δ 72.30, 69.12 (2d, J_{P-P} = 29.8 Hz); MS (*m*/*z*, Ru^{102}) 840.0 (M^+), 565.0 (M^+ − CCPh − PhNCS − CHCN).

Complex **5b** (48% based on **3b**) was similarly prepared from the reaction of *n*-Bu_4NOH with a mixture of **3b** and **4b**. In this reaction **4b** decomposed to give **2**. The products **5b** and **2** were separated by column chromatography. When it was dissolved in solution, complex **5b** transformed to **6b** in ca. 95% yield. Spectroscopic data for **5b**: ^1H NMR ($CDCl_3$) δ 7.82−6.34 (m, 30H, Ph), 4.01 (s, 5H, Cp), 3.82 (s, 1H, CH), 3.27 (s, 3H, OCH_3), 2.65−2.50 (2m, 4H, PCH_2CH_2P); ^{31}P NMR ($CDCl_3$) δ 71.03, 69.98 (2d, J_{P-P} = 30.68 Hz); MS (*m*/*z*, Ru^{102}) 873.0 (M^+), 565.0 (M^+ − CCPh − PhNCS − $CHCO_2CH_3$). Spectroscopic data for **6b**: ^1H NMR ($CDCl_3$) δ 7.71−6.38 (m, 30H, Ph), 5.46 (s, 1H, NH), 3.92 (s, 5H, Cp), 3.07 (s, 3H, OCH_3), 2.02, 1.66 (2m, 4H, PCH_2CH_2P); ^{31}P NMR (−40 °C, $CDCl_3$) δ 69.73, 58.66 (2d, J_{P-P} = 32.2 Hz); ^{13}C NMR ($CDCl_3$) δ 178.6 (CO), 165.4 (s, S*C*N), 143.2−116.3 (Ph and C_α, C_β), 84.5 (Cp), 50.0 (CH_3), 35.4 (t, PCH_2, J_{C-P} = 18.2 Hz), 37.1 (t, PCH_2, J_{C-P} = 20.1 Hz), 15.8 (s, CH); MS (*m*/*z*, Ru^{102}) 873.0 (M^+), 565.0 (M^+ − CCPh − PhNCS − $CHCO_2CH_3$). Anal. Calcd for $C_{49}H_{43}NO_2P_2SRu$ (872.92): C, 67.20; H, 4.91; N, 1.60. Found: C, 66.85; H, 4.92; N, 1.61.

Synthesis of [Ru]−C═C(Ph)C(═NPh)SCH(*p*-C_6H_4CN) (5c) and [Ru]−C═C(Ph)-C(═S)N(Ph)CH(*p*-C_6H_4CN) (7c). To a mixture of **3c** and **4c** (300 mg, 0.301 mmol, **3c**: **4c** = 1:2) in 15 mL of acetone was added *n*-Bu_4NOH (1 mL, 1 M in MeOH). The mixture was stirred at room temperature for 30 min to give a bright yellow solution, and then the volume of the solution was reduced to ca. 3 mL. The residue was then chromatographed on an alumina column. Diethyl ether eluted compound **7c**, and acetone eluted compound **5c**. Removal of the diethyl ether under vacuum give the solid product **7c** (119.4 mg, 0.130 mmol) in 65% yield (based on **4c**). Removal of the acetone gave an oily residue which was washed with 2 × 10 mL of hexane to give [Ru]C═C(Ph)C(═NPh)SCH(*p*-C_6H_4-CN) (**5c;** 68.9 mg, 0.075 mmol) in 75% yield based on **3c**. Complex **5c** in solution transformed to [Ru]C═C(*p*-C_6H_4CN)-SC(NHPh)═CPh (**6c)** in 36 h at room temperature quantitatively. Spectroscopic data for **5c**: ^1H NMR ($CDCl_3$) δ 7.50−6.04 (m, 34H, Ph), 3.77 (s, 5H, Cp), 3.58 (s, CH), 2.85−2.50 (m, 4H, PCH_2CH_2P); ^{31}P NMR ($CDCl_3$) δ 69.31, 67.54 (2d, J_{P-P} = 30.85 Hz); ^{13}C NMR ($CDCl_3$) δ 162.7 (s, S*C*N), 142.6−120.7 (Ph and C_α, C_β), 112.0 (CN), 84.2 (Cp), 30.3, 30.0 (2t, PCH_2-CH_2P, J_{C-P} = 11.0 Hz), 28.3 (s, CH); MS (*m*/*z*, Ru^{102}) 916.2 (M^+), 565.1 (M^+ − CCPh − PhNCS − CHC_6H_4CN). Spectroscopic data for **6c**: ^1H NMR ($CDCl_3$) δ 7.43−6.35 (m, 34H, Ph), 5.84 (s, NH), 3.49 (s, 5H, Cp), 2.45−2.00 (m, 4H, PCH_2CH_2P); ^{31}P NMR ($CDCl_3$) δ 72.15, 66.40 (2d, J_{P-P} = 28.82 Hz); ^{13}C NMR ($CDCl_3$) δ 161.4 (s, S*C*N), 145.4−125.1 (m, Ph and C_α, C_β), 111.5 (CN), 84.5 (Cp), 29.6, 29.2 (2t, PCH_2CH_2P, J_{C-P} = 10.5 Hz); MS (*m*/*z*, Ru^{102}) 916.2 (M^+), 565.1 (M^+ − CCPh − PhNCS − CHC_6H_4CN). Anal. Calcd for $C_{54}H_{44}N_2P_2SRu$ (915.98): C, 70.80; H, 4.84; N, 3.06. Found: C, 70.59; H, 4.48; N, 3.12. Spectroscopic data for **7c**: ^1H NMR ($CDCl_3$) δ 7.67−6.08 (m, 34H, Ph), 3.94 (s, 5H, Cp), 3.09, 2.75 (2m, 5H, CH and PCH_2CH_2P); ^{31}P NMR ($CDCl_3$) δ 94.88, 91.79 (2d, J_{P-P} = 18.27 Hz); ^{13}C NMR ($CDCl_3$) δ 182.0 (CS), 143.4−119.8 (Ph and C_α, C_β), 108.6 (CN), 84.1 (Cp), 31.4, 30.9 (2t, PCH_2CH_2P, J_{C-P} = 15.4 Hz), 28.7 (s, CH); MS (*m*/*z*, Ru^{102}) 917.2 (M^+ + 1), 565.0 (M^+ − CCPh − PhNCS − CHC_6H_4CN). Anal. Calcd for $C_{54}H_{44}N_2P_2SRu$ (915.98): C, 70.80; H, 4.84; N, 3.06. Found: C, 71.29; H, 4.92; N, 2.91.

Synthesis of [Ru]−C═C(Ph)C(═S)N(Ph)CHPh (7d). To a 20 mL CH_2Cl_2 solution of **3d** and **4d** (200 mg, 0.206 mmol, **3d**:**4d** = 6:5) was added NaOMe (55.6 mg, 1.03 mmol). The mixture was stirred at room temperature for 30 min to give an orange-yellow solution. The ^{31}P NMR spectrum of the solution indicated that **4d** disappeared but **3d** was inert. Then the solvent was removed under vacuum and the residue was extracted with 3 × 20 mL of hexane. After filtration, the solvent was removed under vacuum to give the yellow product [Ru]−C═C(Ph)C(═S)N(Ph)CHPh (**7d**; 45.8 mg) in 55% yield based on **4d**. Spectroscopic data for **7d**: ^1H NMR ($CDCl_3$) δ 7.78−6.15 (m, 35H, Ph), 4.87 (s, 5H, Cp), 2.91 (s, H, CH), 2.50−2.15 (m, 4H, PCH_2CH_2P); ^{31}P NMR ($CDCl_3$) δ 92.61, 87.11 (2d, J_{P-P} = 21.7 Hz); ^{13}C NMR ($CDCl_3$) δ 183.4 (S*C*N), 150.3, 146.1−121.8 (Ph, C_α and C_β), 83.6 (Cp), 34.6 (s, CH), 31.4 (t, PCH_2CH_2P, J_{C-P} = 23.4 Hz), 30.3 (t, PCH_2CH_2P, J_{C-P} = 24.5 Hz); MS (*m*/*z*, Ru^{102}) 892.1 (M^+ + 1), 565.0 (M^+ − CCPh − PhNCS − CHC_6H_5). Anal. Calcd for $C_{53}H_{45}NP_2SRu$ (890.98): C, 71.44; H, 5.09; N, 1.57. Found: C, 72.02; H, 4.88; N, 1.52.

Table 3. Crystal and Intensity Collection Data for Cp(dppe)Ru−C(=C(CN)SC(NHPh)=C(Ph)) (6a) and Cp(dppe)Ru−C(=C(Ph)C(=S)N(Ph)CH(*p*-C_6H_4CN)) (7c)

	6a	7c
mol formula	$C_{48}H_{40}N_2P_2RuS$	$C_{54}H_{44}N_2P_2RuS$
space group	$P2_1/n$	$P2_1/n$
cryst syst	monoclinic	monoclinic
a, Å	12.5271(2)	14.6039(4)
b, Å	18.9824(3)	18.9631(6)
c, Å	16.9845(2)	16.7659(5)
β, deg	101.6490(10)	97.503(1)
V, Å^3	3955.63(10)	4603.3(2)
Z	4	4
cryst dimens, mm^3	0.15 × 0.10 × 0.10	0.20 × 0.20 × 0.15
2*θ* range, deg	1.63−26.38	1.63−25.00
indep/total no. of rflns	8094/23 145	8110/19 473
abs coeff, mm^{-1}	0.567	0.494
max/min transmissn	0.8622/0.6919	0.8621/0.7560
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0461	R1 = 0.0438
	wR2 = 0.0829	wR2 = 0.0848
R indices (all data)	R1 = 0.0853	R1 = 0.0850
	wR2 = 0.0969	wR2 = 0.0996
largest diff peak, e Å^{-3}	0.389/−0.433	0.398/−0.408

X-ray Crystal Structure Analysis. The crystal structures of **6a** and **7c** were determined with a Siemens P4 diffractometer equipped with a CCD area detector and controlled by SMART version 4 software. Data reduction was carried out by SAINT version 4 and included profile analysis; this was followed by absorption correction using the program SADABS. Data were collected at 22 °C with Mo Kα radiation. The structures were determined by direct methods and refined using the SHELXTL version 5 package. Hydrogen atoms were introduced in ideal positions, riding on the carbon atom to which they are bonded; each was refined with isotropic temperature factors ranging from 20% to 50% greater than that of the ridden atom. All other atoms were refined with anisotropic thermal parameters. Pertinent crystal data are listed in Table 3.

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Supporting Information Available: Details of the structural determination for complexes **6a** and **7c**, including tables of crystal and intensity collection data, positional and anisotropic thermal parameters, and all of the bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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