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Formation of Organometallic Heterocycles by *S*-alkylated and N-alkylated Ruthenium Vinylidene Complexes

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Treatment of [Ru]C≡CPh (**1**, [Ru] = (η^5-C_5H_5)(dppe)Ru, dppe = $Ph_2PCH_2CH_2PPh_2$) with PhN=C=S at room temperature affords the [2 + 2] cycloaddition product [Ru]-$\overline{C{=}C(Ph)C({=}NPh)S}$ (**2**) which contains a four-membered-ring heterocycle. A series of cationic S-alkylated ruthenium vinylidene complexes $[Ru]{=}C{=}C(Ph)C({=}NPh)SCH_2R^+$ (**3a**, R = $CONH_2$; **3b**, R = $CH{=}CH_2$; **3c**, R = *p*-$C_6H_4CF_3$) and N-alkylated ruthenium vinylidene complexes $[Ru]{=}C{=}C(Ph)C({=}S)N(Ph)CH_2R^+$ (**4b**, R = $CH{=}CH_2$; **4c**, R = *p*-$C_6H_4CF_3$) are prepared from **2** with organic halides at room temperature with high yields. Deprotonation of **3a** and **3c** by *n*-Bu_4NOH in acetone induces novel cyclization reactions *via* C-C bond formation and yields neutral five-membered-ring heterocyclic complexes [Ru]-$\overline{C{=}C(Ph)C({=}NPh)SC}HR$ (**5a**, R = $CONH_2$; **5c**, R = *p*-$C_6H_4CF_3$). In a similar manner, deprotonation of **4b** and **4c** by NaOMe in CH_2Cl_2 also induces another cyclization to yield the pyrrole-2-thione complexes [Ru]-$\overline{C{=}C(Ph)C({=}S)N(Ph)C}HR$ (**6b**, R = $CH{=}CH_2$; **6c**, R = *p*-$C_6H_4CF_3$). At room temperature, **5c** isomerizes to the 2-aminothiophene complex [Ru]-$\overline{C{=}C(p\text{-}C_6H_4CF_3)\ SC(NHPh){=}C}(Ph)$ (**7c**) in solution.

Keywords: Deprotonation-induced cyclization; N-Alkylation vinylidene; *S*-Alkylation vinylidene; Five-membered ring; Heterocyclic; 2-Aminothiophene; Pyrrole-2-thione.

INTRODUCTION

Metal acetylide complexes are active starting materials in organometallic[1-4] and material[5-8] chemistry because of their versatile reactivity. A common reaction observed for acetylide is the [2 + 2] cyclization of the triple bond with unsaturated organic substrates.[9] Cycloaddition with CS_2,[10-12] $(NC)_2C{=}C(CF_3)_2$, and $(NC)_2C{=}C(CN)_2$[13-15] to the acetylide ligand in various metal complexes have been reported. We reported[16] the cycloaddition reactions of the ruthenium acetylide complexes with isothiocyanates RNCS (R = Ph, $PhCH_2$) to afford the complexes with four-member-ring ligands. The relevant reaction mechanisms are explored. In addition, metal vinylidene complexes have been extensively used in synthesis of cyclic metal complexes.[17-21] A study of the reaction of alcohols with ruthenium vinylidene complexes indicated that the electron-withdrawing group either on the acetylide unit or on the metal may facilitate nucleophilic attack on C_α. A CN group at C_γ leads to an intramolecular cycloaddition with the treatment of base.[4,25] It was recently found that the cyclization reactions of S-alkylated and N-alkylated vinylidenes ruthenium that result from the four-membered-ring complex [Ru]-$\overline{C{=}C(Ph)C({=}NPh)S}$ give the neutral heterocyclopentenyl complexes[26] *via* deprotonation. To investigate the details of such reactions, we use organic halides with an electron-withdrawing functional group (XCH_2R, R = $CONH_2$, $CH{=}CH_2$ and *p*-$C_6H_4CF_3$) to explore the selectivity of this kind of deprotonation reaction.

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 three days affords the yellow [2 + 2] cycloaddition product [Ru]-$\overline{C{=}C(Ph)C({=}NPh)S}$ (**2**) in 72% yield.[16] On the basis of the chemical reactivity of **2**,[26] complex **2** apparently can transform into a zwitterionic structure form, by cleavage of the C_α-S bond of the four-membered ring. In the zwitterionic vinylidene the negative charge may reside either at the S atom or at the N atom, thus rendering these atoms nucleophilicity. Indeed, treatment of **2** with ICH_2CONH_2 affords the air-stable cationic vinylidene complex $\{[Ru]{=}C{=}C(Ph)C({=}NPh)SCH_2CONH_2\}[I]$ (**3a**) in 90% yield. The alkylation is found to take place only at the S atom. The vinylidene ligand of **3a** is confirmed by the presence of the triplet of ^{13}C resonance at δ 341.0 with $J_{C\text{-}P}$ = 10.9 Hz, assignable to C_α. The ^{31}P resonance of **3a** appears at δ 77.95 as a singlet due to the fluxional behavior of the vinylidene ligand. Unlike other orange-colored ruthenium vinylidene complexes, **3a** is purple, air-stable, soluble in $CHCl_3$, acetone, THF and insoluble in hexane or ether.

In contrast to the reaction of ICH_2CONH_2, a similar reaction of complex **2** with $ICH_2CH{=}CH_2$ at room temperature affords a mixture of two cationic vinylidene complexes of S-alkylation product $[Ru]{=}C{=}C(Ph)C({=}NPh)SCH_2CH{=}CH_2^+$ (**3b**), as well as an N-alkylation product $[Ru]{=}C{=}C(Ph)C({=}S)N(Ph)CH_2CH{=}CH_2^+$ (**4b**) in a ratio of 6:5 with 78% yield of overall conversion (Scheme I). The ratio of **3b** and **4b** depends on the reaction temperature. The lower the temperature the higher the yield of **3b**. In the reaction of **2** with ICH_2CH CH_2 at 5 °C, the ratio of **3b**:**4b** was 3:2. At room temperature, the ratio was 6:5. Under reflux conditions, the ratio of **3b**:**4b** was found to be approximately 1:1. After the reaction was finished, the ratio of **3b** and **4b** won't change by varying the temperature of the solution. Complexes **3b** and **4b** could not be separated by column chromatography. The ^{31}P NMR spectrum of the mixture formed at room temperature displays two singlet resonances at δ 77.9 and 79.8 in a ratio of 6:5 that are attributed to **3b** and **4b**, respectively. In the ^1H NMR spectrum, two resonances of δ 5.38 and 5.43 are assignable to the Cp groups of **3b** and **4b**, and resonances of δ 3.29 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 341.9 ($J_{C\text{-}P}$ = 13.4 Hz) and 340.2 ($J_{C\text{-}P}$ = 14.6 Hz) are assigned to the C_α carbons of **3b** and **4b**, respectively, indicating that both **3b** and **4b** are vinylidene complexes.

Other vinylidene complexes $[Ru]{=}C{=}C(Ph)C({=}NPh)SCH_2(p\text{-}C_6H_4CF_3)^+$ (**3c**) and $[Ru]{=}C{=}C(Ph)C({=}S)N(Ph)CH_2(p\text{-}C_6H_4CF_3)^+$ (**4c**) were similarly prepared from the reaction of **2** and $BrCH_2(p\text{-}C_6H_4CF_3)$ at room temperature. At room temperature, the ratio of **3c**:**4c** is 4:3 with 83% isolated yield (Scheme I). Spectroscopic data for **3c** and **4c** are consistent with the vinylidene structure and are comparable with those for **3b** and **4b**. Complexes **3c** and **4c** are not separable by column chromatography. However, as described below, pure complexes can be obtained by an indirect route.

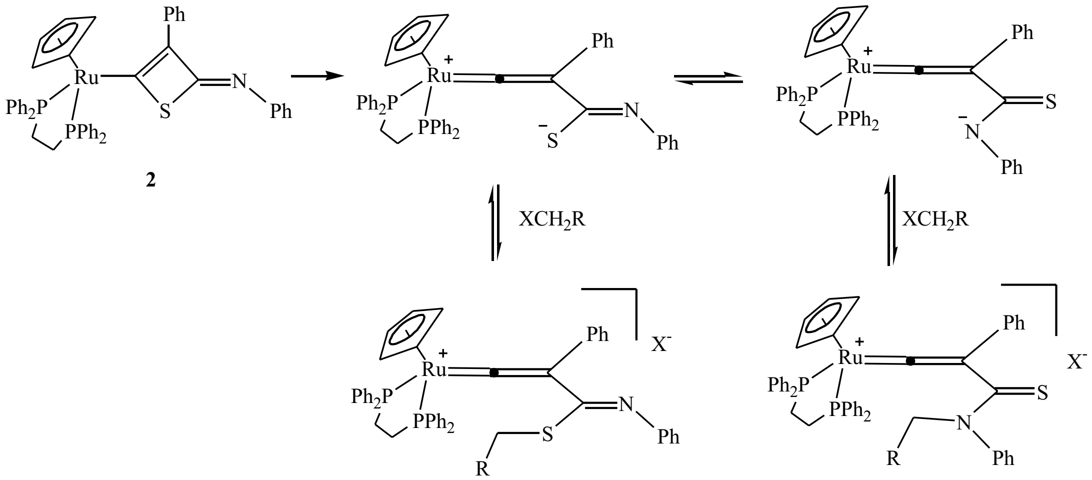
Deprotonation-Induced Cyclization of Vinylidene Complexes 3a

Treatment of **3a** with NaOMe in $CHCl_3$ causes deprotonation of the S-bound methylene group, followed by a cyclization reaction affording a neutral heterocyclopentenyl complex $[Ru]\text{-}\overline{C{=}C(Ph)C({=}NPh)SC}H(CONH_2)$ (**5a**; see Scheme II) in 46% isolated yield. The identification of **5a** in solution was by means of ^{31}P NMR, which shows two doublet resonances at δ 72.56 and 68.54 with $J_{P\text{-}P}$ = 28.93 Hz due to the presence of a stereogenic carbon center in the five-membered ring. Protonation of **5a** in $CHCl_3$ with excess CF_3COOH immediately reverts it back to **3a** in a quantitative yield. Complex **5a** is a yellow, air-stable compound, soluble in $CHCl_3$, moderately soluble in acetone, ether, benzene and insoluble in hexane. It tends to decompose in $CHCl_3$.

Deprotonation-Induced Cyclization of Vinylidene Complex 4b

Treatment of a mixture of **3b** and **4b** in acetone with

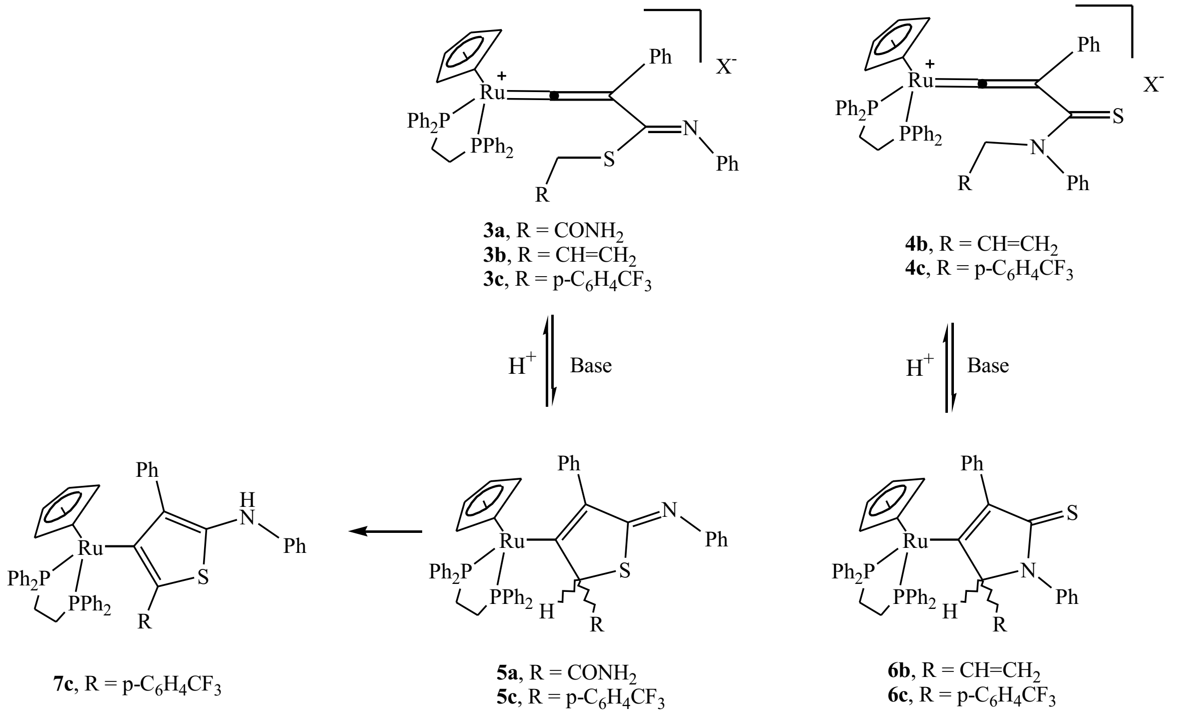
Scheme I



3a, R = $CONH_2$
3b, R = $CH{=}CH_2$
3c, R = $p\text{-}C_6H_4CF_3$

4b, R = $CH{=}CH_2$
4c, R = $p\text{-}C_6H_4CF_3$

Scheme II



n-Bu_4NOH (1M in MeOH) 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 93.28, 87.50 with $J_{P\text{-}P}$ = 23.11 Hz and a singlet resonance at δ 77.9. The former set is attributed to [Ru]-C=C(Ph)C(=S)N(Ph)CH-($CH=CH_2$) (**6b**) and the latter is attributed to complex **3b**. The ratio of **6b** to **3b** is the same as that of **4b** to **3b**, indicating the formation of **6b** is derived from **4b**. No deprotonation reaction of **3b** occurs when either *n*-Bu_4NOH or NaOMe was used, because $CH=CH_2$ is not electron-withdrawing to facilitate the proton abstraction. Complexes **6b** and **3b** were separated by column chromatography. Protonation of **6b** with CF_3COOH immediately gives **4b**.

Deprotonation-Induced Cyclization of Vinylidene Complexes 3c and 4c

Treatment of a mixture of **3c** and **4c** with *n*-Bu_4NOH in acetone causes an immediate color change from purple to yellow. Interestingly, the deprotonation-induced cyclization occurred for both **3c** and **4c**, giving [Ru]-C=C(Ph)C(=NPh)SCH-(*p*-$C_6H_4CF_3$) (**5c**) and [Ru]-C=C(Ph)C(=S)N(Ph)CH(*p*-$C_6H_4CF_3$) (**6c**), respectively (see Scheme II). The ^{31}P NMR spectrum of the reaction mixture displays two pairs of doublet resonances: one appears at δ 69.3 and 66.5 with $J_{P\text{-}P}$ = 30.3 Hz, assignable to **5c**, and the other at δ 93.0 and 87.3 with $J_{P\text{-}P}$ = 22.2 Hz, assignable to **6c**. Both patterns arise from the asymmetric five-membered ring in **5c** and **6c**. Complexes **5c** and **6c** were separated by column chromatography, but **6c** would revert to **4c** either on silica gel or an aluminum oxide column. To a solution of a mixture of **3c** and **4c**, *n*-Bu_4NOH was added and the color of the solution changed from purple-red to bright yellow. Then the solution was reduced to 3 mL and subjected to aluminum packed column chromatography. Diethyl ether eluted **5c**, acetone eluted *n*-Bu_4NOH and methanol eluted an orange band. The orange band was dried under vacuum to give **4c**, which comes from the ring-opening of **6c** with a proton. To the recycled **4c**, CH_2Cl_2 and NaOMe were added and the mixture was stirred for 30 min. The mixture solution was dried under vacuum and extracted with hexane to give pure **6c**. Complex **6c** is stable in air and in solutions, and soluble in CH_2Cl_2, THF, benzene, ether and *n*-hexane. Complex **5c** is stable under -20 °C but transforms to the corresponding 2-aminothiophene complex [Ru]-C=C(*p*-$C_6H_4CF_3$)SC(NHPh)=C(Ph) (**7c**) in solution at room temperature, presumably *via* a hydrogen shift. The ^{31}P NMR spectrum of **7c** displays an AX pattern at δ 71.74, 66.22 with $J_{P\text{-}P}$ = 29.32 Hz. In the ^1H NMR spectrum of **7c**, the Cp resonance appears at δ 3.50 and the NH resonance at δ 4.52. The FAB mass shows that **5c** and **7c** are of the same molecular weight (*m/z* = 959.2).

In the $CHCl_3$ solution of a mixture of **3c** and **4c**, base-induced-deprotonation occurs for **4c** with NaOMe but there is no reaction between **3c** and NaOMe. On the other hand, **5c** can be obtained only by using *n*-Bu_4NOH as proton abstractor. Protonation of **5c** with excess CF_3COOH yielded **3c**. No reaction was observed between complex **7c** and electrophiles such as CF_3COOH, CH_3I and ICH_2CN.

CONCLUSIONS

The facile preparation of neutral five-membered-ring heterocyclic complexes [Ru]-C=C(Ph)C(=NPh)SCHR (**5a,** R = $CONH_2$; **5c**, R = *p*-$C_6H_4CF_3$) and pyrrole-2-thione complexes [Ru]-C=C(Ph)C(=S)N(Ph)CHR (**6b**, R = CH=CH_2; **6c**, R = *p*-$C_6H_4CF_3$) have been achieved by deprotonation of S-bound and N-bound CH_2 units of the cationic vinylidene complexes. A stable neutral 2-aminothiophene complex [Ru]-C=C(*p*-$C_6H_4CF_3$)SC(NHPh)=C(Ph) (**7c**) is formed by hydrogen shift of **5c** in solution. Successful accomplishment of the preparation of S-alkylation and N-alkylation cationic vinylidene complexes with various substituents such as $CONH_2$, CH=CH_2 and *p*-$C_6H_4CF_3$ groups at CH_2 renders this preparation a potentially versatile synthetic method. Facile deprotonation indicates the acidic nature of the methylene protons of **3** and **4**, which may be ascribed to the combined effect of the cationic character and the electron-withdrawing substituents of the vinylidene complexes. There are some reports[22-28] about metal thiofurane and heterocyclic five-membered-ring complexes, but the detailed reactivity is still unknown. We are currently investigating the chemical reactivity of these kinds of heterocyclopentenyl complexes and developing possible asymmetric induction by using the chiral ruthenium center with different phosphine ligands.

EXPERIMENTAL SECTION

General Procedures

All manipulations were performed under nitrogen using vacuum-line, dry box, and standard Schlenk techniques. CH_2Cl_2 was distilled from CaH_2 and diethyl ether and THF from Na/ketyl. All other solvents and reagents were of reagent grade and were used without further purification. NMR spectra were recorded on Bruker AC-200 and AM-300WB FT-NMR spectrometers at room temperature (unless stated otherwise) and are reported in units of δ with residual protons in the solvents as an initial standard ($CDCl_3$, δ 7.24: C_2D_6O, δ 2.04). FAB mass spectra were recorded on a JEOL SX-102A spectrometer. Complex [Ru]-C≡CPh (**1**) and [Ru]-C=C(Ph)C(=NPh)S (**2**) were prepared following the methods reported in the literature.[16] Elemental analyses were carried out at the Regional Center of Analytical Instruments located at National Taiwan University.

Synthesis of {[Ru]=C=C(Ph)C(=NPh)SCH$_2$CONH$_2$}[I] (3a)

To a CH_2Cl_2 (20.0 mL) solution of complex **2** (200 mg, 0.250 mmol), ICH_2CONH_2 (0.10 mL, 0.75 mmol) was added 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 the product {[Ru]=C=C(Ph)C(=NPh)-SCH_2CONH_2}[I] (**3a**) (221.6 mg, 0.225 mmol) in 90% yield. Spectroscopic data of **3a** are as follows: ^1H NMR ($CDCl_3$): δ 7.76-6.23 (m, 30H, Ph), 5.79 (s, NH_2), 5.57 (s, 5H, Cp), 3.34 (s, 2H, CH_2), 2.75-2.50 (m, 4H, PCH_2). ^{31}P NMR ($CDCl_3$): δ 77.95. ^{13}C NMR ($CDCl_3$): δ 341.0 (t, C_α, $J_{C\text{-}P}$ = 10.9 Hz), 170.4 (S*C*N), 133.3-124.5 (Ph), 120.5 (C_β), 93.0 (Cp), 35.0 (CH_2), 28.0 (t, PCH_2, $J_{C\text{-}P}$ = 23.9 Hz). MS (*m/z*, Ru^{102}): 859.0 (M^+-I), 565.0 (M^+-I-organic ligand). Anal. Calcd for $C_{48}H_{43}N_2OP_2SIRu$: C, 58.48; H, 4.40; N, 2.84. Found: C, 58.67; H, 4.37; N, 2.62.

Synthesis of {[Ru]=C=C(Ph)C(=NPh)SCH$_2$CH=CH$_2$}[I] (3b) and {[Ru]=C=C(Ph)C(=S)N(Ph)CH$_2$CH=CH$_2$}[I] (4b)

To a 20 mL CH_2Cl_2 solution of **2** (200 mg, 0.250 mmol), $ICH_2CH=CH_2$ (0.1 mL, 0.75 mmol) was added. The resulting solution was stirred at room temperature for 3 h, then the solvent was reduced to 5 mL. This mixture was slowly added to 60 mL of vigorously stirred diethyl ether. The ^1H and ^{31}P NMR spectra of the mixture indicated formation of the two major products {[Ru]=C=C(Ph)C(=NPh)$SCH_2CH=CH_2$}[I] (**3b**) and {[Ru]=C=C(Ph)C(=S)N(Ph)$CH_2CH=CH_2$}[I] (**4b**). The purple-red precipitate thus formed was filtered and washed with diethyl ether and hexane and dried under vacuum to give **3b** and **4b** (189.0 mg, 0.195 mmol) in a total yield of 78%. The ^{31}P NMR spectra of the crude product displayed the resonances attributed to **3b** and **4b** in a 6:5 ratio. Spectroscopic data of **3b** are as follows: ^1H NMR ($CDCl_3$): δ 7.37-6.27 (m, 30H, Ph), 6.03 (d, 1H, $J_{H\text{-}H}$ = 7.82 Hz, $C\mathit{H}{=}CH\underline{H}_{trans\ to\ H}$), 5.59 (m, 1H, $C\mathit{H}{=}CH_2$), 5.38 (s, 5H, Cp), 5.05 (d, 1H, $J_{H\text{-}H}$ = 7.62 Hz, $C\mathit{H}{=}CH\underline{H}_{cis\ to\ H}$), 3.29 (d, 2H, $J_{H\text{-}H}$ = 6.85 Hz, CH_2), 3.35-2.80 (m, 4H, PCH_2). ^{31}P NMR ($CDCl_3$): δ 77.91. ^{13}C NMR ($CDCl_3$): δ 341.9 (t, C_α, $J_{C\text{-}P}$ = 13.4 Hz), 153.6 (S*C*N), 150.1 (*C*H=CH_2), 136.7-121.0 (Ph, C_β), 93.2 (Cp), 92.2 (CH=*C*H_2), 28.4 (PCH_2, PCH_2, $J_{C\text{-}P}$ = 23.8 Hz), 17.4

(CH_2). MS (*m/z*, Ru^{102}): 842.1 (M^+-I), 565.1 (M^+-I-organic ligand). Spectroscopic data of **4b** are as follows: ^1H NMR ($CDCl_3$) δ 7.54-6.62 (m, 35H, Ph), 6.03 (d, 1H, $J_{H\text{-}H}$ = 7.82Hz, $C\mathit{H}{=}CH\underline{H}_{\text{trans to }H}$), 5.59 (m, 1H, $C\mathit{H}{=}CH_2$), 5.43 (s, 5H, Cp), 5.05 (d, 1H, $J_{H\text{-}H}$ = 7.62 Hz, $C\mathit{H}{=}CH\underline{H}_{\textit{cis to H}}$), 3.43 (d, 2H, CH_2, $J_{H\text{-}H}$ = 6.78 Hz), 3.25-2.75 (m, 4H, PCH_2). ^{31}P NMR ($CDCl_3$): δ 79.79. ^{13}C NMR ($CDCl_3$): δ 340.2 (t, C_α, $J_{C\text{-}P}$ = 14.6 Hz), 185.1 (*C*S), 143.7 (*C*H=CH_2), 138.4-119.7 (Ph and C_β), 93.0 (Cp), 90.9 (CH=*C*H_2), 59.2 (CH_2), 28.2 (t, PCH_2, $J_{C\text{-}P}$ = 23.8 Hz). MS (*m/z*, Ru^{102}) 842.1 (M^+-I), 565.0 (M^+-I-organic ligand). Anal. Calcd for $C_{49}H_{44}NP_2SIRu$: C, 60.74; H, 4.58; N, 1.45. Found: C, 60.97; H, 4.51; N, 1.37.

Complexes {[Ru]=C=C(Ph)C(=NPh)SCH_2(*p*-$C_6H_4CF_3$)}[Br] (**3c**) and {[Ru]=C=C(Ph)C(=S)N(Ph)CH_2(*p*-$C_6H_4CF_3$)}[Br] (**4c**) (**3c**:**4c** = 4:3, 83% total yield), were prepared using the same procedure as that for **3b** and **4b**. Spectroscopic data of **3c** are as follows: ^1H NMR ($CDCl_3$): δ 7.54-6.20 (m, 34H, Ph), 5.41 (s, 5H, Cp), 3.28 (s, 2H, CH_2), 2.85-2.50 (m, 4H, PCH_2). ^{31}P NMR ($CDCl_3$): δ 78.01. ^{13}C NMR ($CDCl_3$): δ 347.7 (t, C_α, $J_{C\text{-}P}$ = 14.6 Hz), 186.3 (S*C*N), 140.3-120.5 (Ph, *C*F_3, C_β), 93.1 (Cp), 30.0 (CH_2), 28.8 (t, PCH_2, $J_{C\text{-}P}$ = 21.9 Hz). MS (*m/z*, Ru^{102}): 960.2 (M^+-I), 565.1 (M^+-I-organic ligand). Spectroscopic data of **4c** are as follows: ^1H NMR ($CDCl_3$): δ 7.58-6.08 (m, 34H, Ph), 5.44 (s, 5H, Cp), 3.37 (s, 2H, CH_2), 3.20-2.70 (m, 4H, PCH_2). ^{31}P NMR ($CDCl_3$): δ 79.84. ^{13}C NMR ($CDCl_3$): δ 347.3 (t, C_α, $J_{C\text{-}P}$ = 15.8 Hz), 200.4 (CS), 139.4-122.2 (Ph , *C*F_3, C_β), 92.5 (Cp), 29.7 (CH_2), 28.3 (t, PCH_2, $J_{C\text{-}P}$ = 20.7 Hz). MS (*m/z*, Ru^{102}): 942.2 (M^+-Br), 565.0 (M^+-Br-organic ligand). Anal. Calcd for $C_{54}H_{45}NP_2SF_3BrRu$: C, 62.37; H, 4.36; N, 1.35. Found: C, 62.58; H, 4.28; N, 1.27.

Synthesis of $[\mathrm{Ru}]\text{-}\overline{\mathrm{C{=}C(Ph)S({=}NPh)C}}\mathrm{HCONH_2}$ (5a)

To a 15 mL acetone solution of **3a** (300 mg, 0.310 mmol), *n*-Bu_4NOH (1 mL, 1 M in MeOH) was added. The mixture was stirred at room temperature for 30 min to give a bright yellow solution and then the solvent was removed to 3.0 mL. The residue was subjected to aluminum oxide packed column chromatography. The yellow product was eluted with benzene. Removal of benzene solvent followed by addition of hexane gave a yellow precipitate. After filtration, the solid was further washed with 10 mL of hexane and gave the product $[\mathrm{Ru}]\text{-}\overline{\mathrm{C{=}C(Ph)S({=}NPh)C}}\mathrm{HCONH_2}$ (**5a**, 120.1 mg, 0.140 mmol) in 46% yield. Spectroscopic data of **5a** are as follows: ^1H NMR ($CDCl_3$): δ 7.90-6.37 (m, 32H, Ph), 5.16 (s, 1H, CH), 4.73 (br., 2H, NH_2), 4.01 (s, 5H, Cp), 2.35-2.10 (m, 4H, PCH_2). ^{31}P NMR ($CDCl_3$): δ 72.56, 68.54 (2d, $J_{P\text{-}P}$ = 28.93 Hz). ^{13}C NMR ($CDCl_3$): δ 174.8 (CO), 154.9 (S*C*N), 142.0-121.3 (Ph and C_β), 134.5 (t, C_α, $J_{C\text{-}P}$ = 6.6 Hz), 84.9 (Cp), 31.9 (dd, PCH_2, $^1J_{C\text{-}P}$ = 15.4 Hz, $^2J_{C\text{-}P}$ = 3.5 Hz) , 32.0 (dd, PCH_2, $^1J_{C\text{-}P}$ = 15.7 Hz, $^2J_{C\text{-}P}$ = 2.4 Hz), 31.4 (s, CH). MS (*m/z* , Ru^{102}): 858.2 (M^+), 565.0 (M^+-organic ligand). Anal. Calcd for $C_{48}H_{42}N_2OP_2SRu$: C, 67.20; H, 4.93; N, 3.27. Found: C, 67.83; H, 4.69; N, 3.05.

Synthesis of $[\mathrm{Ru}]\text{-}\overline{\mathrm{C{=}C(Ph)C({=}S)N(Ph)C}}\mathrm{HCH{=}CH_2}$ (6b)

To a 20 mL CH_2Cl_2 solution of a mixture of **3b** and **4b** (200 mg, 0.206 mmol, **3b**:**4b** = 6:5) NaOMe (55.6 mg, 1.03 mmol) was added. The mixture was stirred at room temperature for 30 minutes to give an orange-yellow solution and then the solvent was removed under vacuum. The residue was extracted with 20 mL of hexane three times. The extracted solution was filtered, and the solvent was removed under vacuum to give the yellow precipitate $[\mathrm{Ru}]\text{-}\overline{\mathrm{C{=}C(Ph)C({=}S)N(Ph)C}}\mathrm{HCH{=}CH_2}$ (**6b**, 37.7 mg, 0.045 mmol) in 19% yield (42% yield based on **4b**). Spectroscopic data of **6b** are as follows: 1H NMR ($CDCl_3$): δ 7.96-6.60 (m, 30H, Ph), 4.97 (s, 5H, Cp), 3.35 (d, H, CH, $J_{H\text{-}H}$ = 9.04 Hz), 2.45-2.10 (m, 4H, PCH_2CH_2P). ^{31}P NMR ($CDCl_3$): δ 93.28, 87.50 (2d, $J_{P\text{-}P}$ = 23.11 Hz). ^{13}C NMR ($CDCl_3$): δ 188.1 (S*C*N), 146.6 (*C*H=CH_2), 137.7-122.6 (Ph, C_α and C_β), 105.2 (CH=*C*H_2), 83.7 (Cp), 30.1 (t, PCH_2, $J_{C\text{-}P}$ = 32.6 Hz), 29.3 (t, PCH_2, $J_{C\text{-}P}$ = 30.7 Hz), 29.7 (s, CH). MS (*m/z*, Ru^{102}): 842.1 (M^++1), 565.0 (M^+-organic ligand). Anal. Calcd for $C_{49}H_{43}NP_2SRu$: C, 69.98; H, 5.15; N, 1.67. Found: C, 70.12; H, 5.03; N, 1.54.

Synthesis of $[\mathrm{Ru}]\text{-}\overline{\mathrm{C{=}C(Ph)C({=}NPh)SC}}\mathrm{H}(p\text{-}\mathrm{C_6H_4CF_3})$ (5c), $[\mathrm{Ru}]\text{-}\overline{\mathrm{C{=}C(Ph)C({=}S)N(Ph)C}}\mathrm{H}(p\text{-}\mathrm{C_6H_4CF_3})$ (6c) and $[\mathrm{Ru}]\text{-}\overline{\mathrm{C{=}C}(p\text{-}\mathrm{C_6H_4CF_3})\mathrm{SC(NHPh){=}C}}\mathrm{(Ph)}$ (7c)

To a solution of a mixture of **3c** and **4c** (400 mg, 0.385 mmol, **3c**:**4c** = 4:3) in 10 mL of acetone, *n*-Bu_4NOH (0.5 mL, 1 M in MeOH) was added. The mixture was stirred at room temperature for 30 min to give a bright yellow solution and then the solution was reduced to 3 mL. The residue was subjected to aluminum packed column chromatography. Diethyl ether eluted a yellow band, acetone eluted the base and methanol eluted an orange band. The yellow band was dried under vacuum and the residue was washed with 2 × 10 mL of hexane and dried under vacuum to give the product $[\mathrm{Ru}]\text{-}\overline{\mathrm{C{=}C(Ph)S({=}NPh)C}}\mathrm{H}(p\text{-}\mathrm{C_6H_4CF_3})$ (**5c**, 118.0 mg, 123 mmol) in 32% yield (56% yield based on **3c**). Complex **5c** transformed to $[\mathrm{Ru}]\text{-}\overline{\mathrm{C{=}C}(p\text{-}\mathrm{C_6H_4CF_3})\mathrm{SC(NHPh){=}C}}\mathrm{(Ph)}$ (**7c**) in 36 hr in solution at room temperature. The orange band was dried under vacuum to give the un-reacted **4c** and base. In a Schlenk flask charged with recycled **4c** and base, CH_2Cl_2 and NaOMe were added and the mixture was stirred at room temperature for 30 minutes and the color changed from orange to yellow. The solvent was removed under vacuum. The residue was extracted with 20 mL of hexane three times. The extracted solution was filtered, and the solvent was removed under vacuum to give the yellow precipitate $[Ru]-\overline{C=C(Ph)C(=S)N(Ph)C}H(p-C_6H_4CF_3)$ (**6c**, 81.2 mg, 0.084 mmol) in 22% yield (51% yield based on **4c**). Spectroscopic data of **5c** are as follows: ^1H NMR ($CDCl_3$): δ 7.46-6.57 (m, 30H, Ph), 3.57 (s, 5H, Cp), 4.39 (s, CH), 2.40-2.10 (2m, 4H, PCH_2CH_2P). ^{31}P NMR ($CDCl_3$): δ 69.35, 66.45 (2d, $J_{P\text{-}P}$ = 30.30 Hz). ^{13}C NMR ($CDCl_3$): δ 173.2 (S*C*N), 154.7-112.9 (Ph, C_α, *C*F_3, C_β), 84.4 (Cp), 31.6 (dd, PCH_2, $^1J_{C\text{-}P}$ = 30.2 Hz, $^2J_{C\text{-}P}$ = 15.1 Hz), 30.6 (dd, PCH_2, $^1J_{C\text{-}P}$ = 32.0 Hz, $^2J_{C\text{-}P}$ = 16.0 Hz), 22.3 (CH). MS (*m/z*, Ru^{102}): 959.2 (M^+), 565.1 (M^+-organic ligand). Spectroscopic data of **6c** are as follows: ^1H NMR ($CDCl_3$): δ 7.95-6.55 (m, 34H, Ph), 4.93 (s, 5H, Cp), 3.20 (s, H, CH), 2.40-2.05 (m, 4H, PCH_2CH_2P). ^{31}P NMR ($CDCl_3$): δ 92.98, 87.33 (2d, $J_{P\text{-}P}$ = 22.17 Hz). MS (*m/z*, Ru^{102}): 960.1 (M^++1), 565.0 (M^+-organic ligand). Spectroscopic data of **7c** are as follows: ^1H NMR ($CDCl_3$) δ 7.53-6.60 (m, 34H, Ph), 3.50 (s, 5H, Cp), 4.52 (s, CH), 2.65-2.50 (2m, 4H, PCH_2CH_2P). ^{31}P NMR ($CDCl_3$): δ 71.74, 66.22 (2d, $J_{P\text{-}P}$ = 29.32 Hz). ^{13}C NMR ($CDCl_3$): δ 193.3 (S*C*N), 157.0-124.6 (m, Ph and CF_3), 121.9 (C_β), 133.8 (t, C_α, $J_{C\text{-}P}$ = 5.9 Hz), 84.6 (Cp), 33.2 (dd, PCH_2, $^1J_{C\text{-}P}$ = 32.9Hz, $^2J_{C\text{-}P}$ = 17.5 Hz), 32.0 (dd, PCH_2, $^1J_{C\text{-}P}$ = 32.0 Hz, $^2J_{C\text{-}P}$ = 16.2 Hz), 22.3 (CH). MS (*m/z*, Ru^{102}): 959.2 (M^+), 565.1 (M^+-organic ligand). Anal. Calcd for $C_{54}H_{44}NP_2SF_3Ru$: C, 67.63; H, 4.93; N, 3.27. Found: C, 68.15; H, 4.87; N, 3.15.

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