Synthesis of (Vinylidene)- and (Cyclopropenyl)ruthenium Complexes Containing a Tris(pyrazolyl)borato (Tp) Ligand

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A convenient high-yield route to [Ru(C≡C–Ph)(Tp)(PPh_3)$_2$] [**2**; Tp = HB(pz)$_3$, pz = pyrazolyl] has been found through the intermediacy of [$RuCl_2$(Hpz)$_2$(PPh_3)$_2$] (**1**). This complex is readily obtained on treatment of [$RuCl_2(PPh_3)_3$] with 2 equiv. of pyrazole in boiling THF. The molecular structures of complexes **1** and **2** have been confirmed by single-crystal X-ray diffraction analysis. A number of new cationic vinylidene complexes [Ru{=C=C(Ph)CH_2R}(Tp)(PPh_3)$_2$]$^+$ [**3a**, R = CN; **3b**, R = HC=CH_2; **3c**, R = CH=C(CH_3)$_2$; **3d**, R = Ph; **3e**, R = C(O)OMe] have been prepared by electrophilic addition of organic halides to complex **2**. The deprotonation reaction of **3a** yields the cyclopropenyl complex **4a**. One phosphane ligand of **4a** is remarkably labile, being replaced by donor ligands L to yield diastereomeric mixtures of the cyclopropenyl complexes **5a**–**5d** mostly in an approximate 4:1 ratio. The cyclopropenyl rings in **4a** and **5a** are susceptible to ring opening by I_2. In addition, treatment of **4a** with *n*BuNC in the presence of MeOH results in substitution of a phosphane ligand by *n*BuNC followed by protonation of the three-membered ring by MeOH. This is then followed by addition of methoxide to give the vinyl ether complex [Ru{C(OMe)=C(Ph)CH_2CN}(Tp)(PPh_3)(*n*BuNC)] (**8a**).

Introduction

The hydrotris(pyrazol-1-yl)borate (Tp) ligand has been used to stabilize a wide variety of transition-metal complexes since its discovery by Trofimenko,[1] and the development of Tp chemistry within group VIII, in particular, has accelerated recently.[1c,1d] Tp is often compared with Cp (η^5-C_5H_5) due to the same charge and number of electrons donated, although their differences in size and electronic properties are obvious. Thus, the cone angle of Tp (close to 180°) is well above the value of 100° calculated for Cp. The steric bulkiness of the Tp ligand appears to disfavor higher coordination numbers or bulky metal fragment. Much of the chemistry of the [CpRu(PPh_3)$_2$]$^+$ fragment can be traced to the strongly π-basic nature of the ruthenium center. Replacing Cp with Tp increases the basicity of the metal center further, and it has been claimed that it also leads to more ideally octahedral hybridization.[2] The chemistry of (vinylidene)transition-metal complexes has attracted increasing attention in recent years especially because of their application as key intermediates in stoichiometric and catalytic transformations of organic molecules.[3] Representative examples of ruthenium-based catalysis involving vinylidene complexes have been reported for the cyclization of dienylalkynes,[4a] the dimerization of HC≡C*t*Bu,[4b] and the tandem cyclization/reconstructive addition of propargyl alcohols with allyl alcohols.[4c] A key characteristic of vinylidene complexes appears to be the electrophilicity of the α-carbon atom, which adds, often easily, amines,[5] alcohols,[6,7] phosphanes,[8] and even fluoride.[6a]

The reactions of metal complexes with cyclopropenes often generate interesting chemistry, mainly due to the large amount of strain energy (ca. 50 kcal/mol) in the three-membered ring.[9] This molecule has played a crucial role in the development of the important concept of aromaticity, and its chemical reactivity has been extensively explored.[10] The syntheses of cyclopropenyl-containing metal derivatives in which the metal atom is bonded to the sp^3-hybridized carbon atom of the cyclopropene ring have been reported in the literature.[11] However, only a few examples of such derivatives in which the metal atom is bonded to the sp^2-carbon atom of the three-membered ring have been reported.[12] A few structurally different (cyclopropenylidene)-transition-metal complexes, mostly prepared from dichlorocyclopropene,[13] and a number of π-cyclopropene complexes,[14] are also known.

During the course of our investigations into (vinylidene)ruthenium chemistry, we previously studied the formation of several interesting neutral cyclopropenyl complexes.[6] For example, the cationic complex [RuCp{=C=C(Ph)CH_2CN}(PPh_3)$_2$]$^+$ was found to undergo deprotonation to afford the yellow cyclopropenyl complex. The cationic nature of the vinylidene complex, along with the presence of an electron-withdrawing functionality such as a CN group at C-γ of the vinylidene ligand, play a role in enhancing the acidity of the proton next to the CN group. Thus, addition of a base successfully brings about an intra-

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molecular cycloaddition leading to the formation of a neutral cyclopropenyl complex. To elaborate the breadth of such a system, we set out to study analogous ruthenium complexes containing a Tp ligand. Herein, we report the synthesis of a series of new cationic vinylideneruthenium complexes and new neutral cyclopropenyl complexes in high yields. The reaction of the cyclopropenyl complex with I_2 to give a new vinylidene complex is also reported.

Results and Discussion

Preparation of (Tp)metal Acetylide Complexes

We have previously reported[6b] that $[RuCl(Tp)(PPh_3)_2]$ reacts with phenylacetylene in the presence of NaOMe to afford the acetylide complex $[Ru(C{\equiv}C{-}Ph)(Tp)(PPh_3)_2]$ (**2**). However, complex **2**, prepared using this method, is persistently contaminated with the starting material because of incomplete conversion. Therefore, a new synthetic approach to prepare **2** has been developed (Scheme 1). This new, convenient, high-yield route to **2** proceeds through the intermediacy of $[RuCl_2(Hpz)_2(PPh_3)_2]$ (**1**) (Hpz = pyrazole). This compound is readily obtained as an air-sensitive yellow solid in 97% yield upon treatment of $[RuCl_2(PPh_3)_3]$ with 2 equiv. of pyrazole in boiling THF for 1 h. Complex **1** is soluble in $CHCl_3$, CH_2Cl_2, MeOH, CH_3CN and THF but insoluble in hexane, and was characterized by a combination of elemental analysis and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. Characteristic ^1H NMR spectroscopic data for **1** include a singlet at $\delta = 11.67$ ppm assignable to the proton of the pyrazole ligand. In addition, the solid-state structure was determined by a single-crystal X-ray diffraction study. An ORTEP diagram is shown in Figure 1 (with selected bond lengths and angles). The coordination geometry of **1** is approximately octahedral with both pyrazole ligands *N*-bonded. The ruthenium atom is at the center, with the nitrogen atoms of the two pyrazole ligands and two PPh_3 ligands occupying the equatorial positions and the axial positions being occupied by two *trans*-chlorine atoms. The Ru−N(1) and Ru−N(3) bond lengths are 2.133(5) and 2.127(5) Å, respectively. The two Ru−Cl bonds of 2.428(2) and 2.426(2) Å are similar to those found in other (pyrazole)ruthenium complexes, such as 2.427(2) and 2.392(2) Å in $[RuCl_2(HPz)(DMSO)_3]$ and 2.427(1) and 2.397(1) Å in $[RuCl_2(HPz)_2(DMSO)_2]$.[15] Pyrazoles and their deprotonated form (pyrazolate anions) are attractive ligands that exhibit a rich coordination chemistry.[16] Pyrazoles and substituted pyrazoles usually behave as monodentate ligands[17] and these monodentate pyrazoles may give rise to interesting processes such as prototropic equilibrium or reversible metal−ligand binding, which are relevant to biological systems.[18]

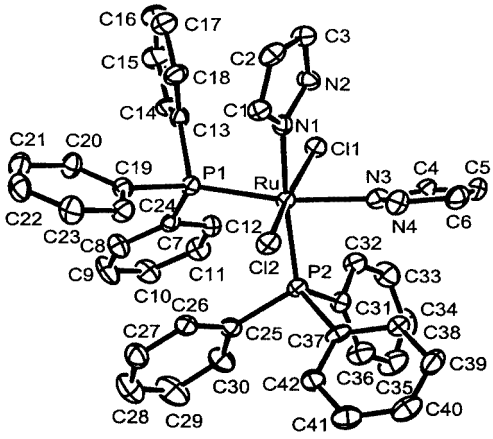
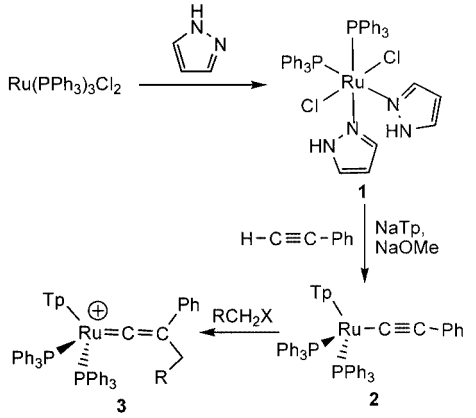


Figure 1. ORTEP drawing of complex **1** (30% probability ellipsoids); selected bond lengths [Å] and angles [°]: Ru−P(1) 2.3423(20), Ru−P(2) 2.3421(20), Ru−N(1) 2.133(5), Ru−N(3) 2.127(5), Ru−Cl(1) 2.4283(19), Ru−Cl(2) 2.4261(19); N(1)−Ru−N(3) 83.24(20)

The one-pot reaction of **1** with NaTp and phenylacetylene in the presence of NaOMe gives the ruthenium acetylide complex $[Ru(C{\equiv}C{-}Ph)(Tp)(PPh_3)_2]$ (**2**). The yield of this one-pot reaction was higher than the yield obtained from the previously reported reaction that required several steps.[6b] The ν(B−H) vibration of **2** is found at 2489 cm^{-1}, which is characteristic of Tp bound to a metal center in a terdentate (N,N,N) manner. Yellow crystals of **2** were obtained by slow diffusion of hexane into a $CHCl_3$ solution of **2** at room temperature for 3 d. The molecular structure of **2** was determined by an X-ray diffraction study. An ORTEP diagram is shown in Figure 2 (with selected bond lengths and angles). The coordination geometry of complex **2** is approximately octahedral. The Ru−C(1) bond length of 2.006(6) Å is typical of an Ru−C single bond. The Ru−C(1)−C(2) bond angle of 173.9(5)° and C(1)−C(2) bond length of 1.205(8) Å are characteristic of a ruthenium acetylide complex.



Scheme 1

Cationic (Tp)(vinylidene)metal Complexes

Treatment of **2** with ICH_2CN affords the cationic vinylidene complex $[Ru\{{=}C{=}C(Ph)CH_2CN\}(Tp)(PPh_3)_2]I$ (**3a**) in 90% yield (Scheme 1).[9b] In the presence of excess NH_4PF_6 the counteranion is replaced by PF_6^-. Similarly,

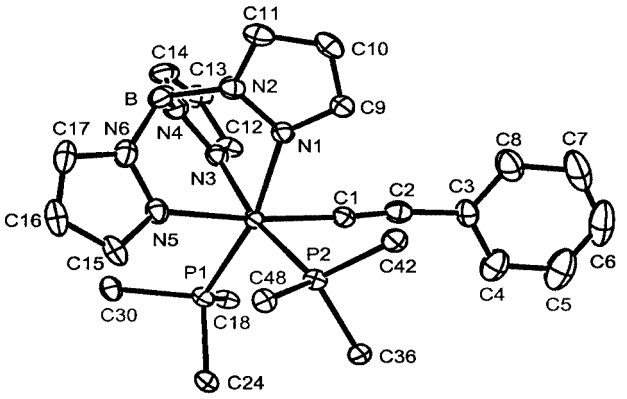
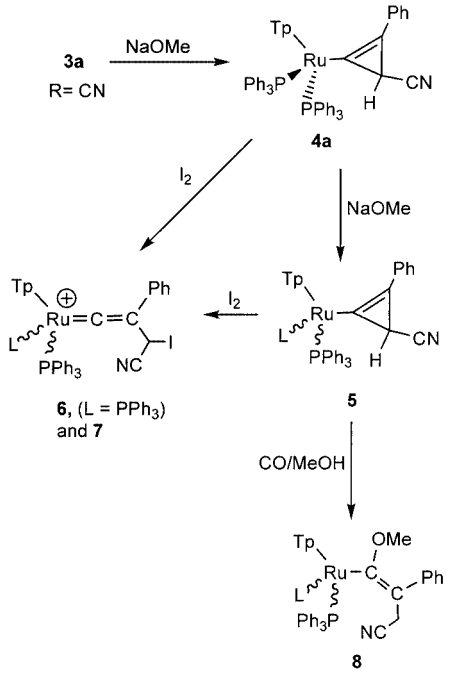


Figure 2. ORTEP drawing of complex **2** (30% probability ellipsoids); the carbon atoms of the phenyl groups (except the *ipso*-carbon atoms) on the triphenylphosphane have been eliminated for clarity; selected bond lengths [Å] and angles [°]: Ru−C(1) 2.006(6), C(1)−C(2) 1.205(8), C(2)−C(3) 1.439(9); Ru−C(1)−C(2) 173.9(5), C(1)−C(2)−C(3) 167.8(6)

the preparation of other vinylidene complexes $[Tp(PPh_3)_2Ru{=}C{=}C(Ph)CH_2R]^+$ [**3b**, R = CH=CH_2; **3c**, R = CH=$C(CH_3)_2$; **3d**, R = Ph; **3e**, R = C(O)OMe] was accomplished by treating **2** with the corresponding halides; they were all isolated in high yields. With the exception of **3e**, all the vinylidene complexes mentioned above were prepared in CH_2Cl_2 at room temperature; mild heating was required for the synthesis of **3e**, and a mixture of CH_2Cl_2/$CHCl_3$ (3:1, v/v) was used as solvent in order to achieve a slightly higher reaction temperature. Complexes **3a**−**3e** are all soluble in polar solvents such as $CHCl_3$, CH_2Cl_2, MeOH and CH_3CN but insoluble in acetone, diethyl ether and hexane. These complexes are green in the solid state. Characteristic spectroscopic data of theses vinylidene complexes consist of a strongly deshielded C-α resonance as a triplet at $\delta = 370 \pm 5$ ppm in the ^{13}C NMR spectrum and a singlet ^{31}P NMR resonance at $\delta = 36 \pm 1$ ppm in $CDCl_3$ at room temperature; this is due to the fluxional behavior of the vinylidene ligand.[19] The spectroscopic data of the Cp analogues are similar; the triplet C-α resonance appears at $\delta = 340 \pm 5$ ppm in the ^{13}C NMR spectrum and a singlet ^{31}P NMR resonance is observed at $\delta = 42 \pm 1$ ppm. The newly formed carbon−carbon bond of these vinylidene complexes is easily cleaved in the presence of acid. Complexes **3a**−**3d** are all stable at room temperature for a period of 3 d, after which they decomposed to give unidentified products.

(Cyclopropenyl)(Tp)metal Complexes

The neutral complex $[Ru\{C{=}C(Ph)CH(CN)\}(Tp)(PPh_3)_2]$ (**4a**) can be readily prepared in high yield by deprotonation of **3a** at 0 °C in CH_2Cl_2 (Scheme 2). However, no deprotonation was observed for the other vinylidene complexes **3b**−**3d**, even in the presence of NaOMe, nBu_4NF (1 M in THF), DBU (1,8-diazabicyclo[5.4.0]undecene) or KOH (dissolved in a minimum amount of H_2O) at room temperature for 24 h. We have previously prepared neutral cyclopropenyl complexes containing a Cp ligand by deprotonation of the cationic vinylidene precursors.[19] Cyclopropenyl complexes with substituents such as vinyl, dimethylvinyl, phenyl and methyl ester groups are all achievable. The chemistry of the $[CpRu(PPh_3)_2]^+$ fragment can be traced to the strongly π-basic nature of the ruthenium center. Replacing Cp with Tp increases the basicity of the metal center and reduces the cationic character of the vinylidene complexes. Complexes **3b**−**3e** all lack enough cationic character to lead to intramolecular cycloaddition. We thus believe that the facile deprotonation of cationic vinylidene complexes may be ascribed to the combined effect of the cationic character and the presence of the electron-withdrawing substituent of the vinylidene complex.



Scheme 2

The analogous Cp complex of **4a** is stable with respect to ligand substitution — the phosphane ligand binds strongly to the ruthenium center, making the coordination site unavailable for an incoming substrate. In contrast, the Tp complex **4a** is susceptible to ligand substitution under relatively mild conditions. This may be attributed to the increased steric bulkiness of the Tp ligand relative to Cp. For example, when 2 equiv. of PhCN, *p*-$CF_3C_6H_4CN$, *n*BuNC or *t*BuNC were added at room temperature to a CH_2Cl_2 solution of **4a** a smooth reaction ensued over 1 h which afforded good yields of the bright-yellow (cyclopropenyl)ruthenium complexes $[Ru\{C{=}C(Ph)CH(CN)\}(Tp)(PPh_3)(L)]$ (**5a**, L = *n*BuNC; **5b**, L = *t*BuNC; **5c**, L = *p*-$CF_3C_6H_4CN$; **5d**, L = PhCN), respectively (Scheme 2). Significantly, when these reactions were repeated using only 1 equiv. of L much lower yields (ca. 8%) were obtained.

Complexes **5a**−**5d** all contain two diastereomers in a 4:1 ratio. The ^1H NMR resonances of **5a** attributed to the CHCN moiety of the three-membered rings of the major and the minor isomers appear at $\delta = 0.93$ and 1.16 ppm,

respectively. In the $^{13}C\{^1H\}$ NMR spectrum, singlet ^{13}C resonances at δ = 3.8 and 3.5 ppm and doublet resonances at δ = 128.7 and 128.8 ppm, with $^2J_{P,C}$ coupling constants of 11.6 and 11.5 Hz, are assigned to the CHN and the ruthenium-bonded C-α carbon atoms of the major and the minor isomers, respectively. Interestingly, in the cases of **5c** and **5d** the major isomer is more stable than the minor isomer; the minor isomer decomposes within about 3 h.[6b] In the $^{13}C\{^1H\}$ NMR spectrum of **5c**, the singlet resonance at δ = 4.10 ppm and the doublet resonance at δ = 132.6 ppm, with a $^2J_{P,C}$ coupling of 12.3 Hz, are assigned to the CHN and the ruthenium-bonded C-α carbon atoms of the major isomer; the ^{13}C NMR spectrum of the minor isomer was not obtained because of its lower stability. Complexes **5a** and **5b** are stable in diethyl ether and THF, but in $CHCl_3$ compounds **5b**, **5c**, **5d** are less stable than **5a**. Furthermore, **5b** decomposes in $CHCl_3$ producing [RuCl(Tp)(PPh_3)(*t*BuNC)] and some unidentified organic products. Decomposition of **5c** and **5d** produces complicated mixtures. The stability of the substituted cyclopropenyl complexes was found to decrease in the order *n*BuNC > *t*BuNC > *p*-$CF_3C_6H_4CN$ > PhCN.

Opening of the Three-Membered Ring by Electrophiles

Treatment of **4a** with I_2 at 0 °C afforded the cationic vinylidene complex [Ru{=C=C(Ph)CH(I)(CN)}(Tp)(PPh_3)$_2$]I (**6**) in 79% yield (Scheme 2). Complex **6** is a green solid and its spectroscopic data display the features of a vinylidene complex. The pattern of two-doublet resonances at δ = 34.3 and 33.6 ppm, with a $J_{P,P}$ coupling of 26.9 Hz, in the ^{31}P NMR spectrum arises from the stereogenic C-γ center. In the ^1H NMR spectrum of **6** the resonance at δ = 3.23 ppm is assigned to the CHICN group, and in the $^{13}C\{^1H\}$ spectrum the triplet resonance at δ = 374.5 ppm, with a $^2J_{P,C}$ coupling of 15.1 Hz, is assigned to the vinylidene C-α atom. Similarly, treatment of **5a** with I_2 affords the addition product [Ru{=C=C(Ph)CH(I)(CN)}(Tp)(PPh_3)(*n*BuNC)]I (**7**) in high yield. Interestingly, only one diastereoisomer is observed for **7**. The ^1H NMR spectrum of **7** displays one singlet resonance at δ = 3.56 ppm, assigned to the CHICN group; the doublet resonance at δ = 367.3 ppm, with a $^2J_{P,C}$ coupling of 16.4 Hz, in the ^{13}C NMR spectrum is assigned to the vinylidene C-α atom. Formation of these vinylidene complexes occurs by selective cleavage of the cyclopropenyl single bond near the metal center. No alkylation is observed when **4a** is treated with CH_3I, CH_3CH_2I, CH_2=$CHCH_2Br$, CH≡$CHCH_2Br$ or ICH_2CN.

Reaction of 4a with nBuNC in the Presence of MeOH

Reaction of **4a** with *n*BuNC in the presence of MeOH causes substitution of a phosphane ligand by *n*BuNC. This is followed by protonation of the three-membered ring to give a vinylidene intermediate and addition of MeO^- to give the vinyl ether complex [Ru{C(OMe)=C(Ph)CH_2CN}(Tp)(PPh_3)(*n*BuNC)] (**8a**). Similarly, the reaction of **4a** with *t*BuNC in the presence of MeOH gives the vinyl ether product [Ru{C(OMe)=C(Ph)CH_2CN}(Tp)(PPh_3)(*t*BuNC)] (**8b**) in lower yield, which may be due to steric effects. The ^1H NMR spectrum of **8a** displays an AB pattern for the CH_2CN moiety, with two doublets centered at δ = 3.86 and 2.79 ppm with a coupling constant of 16.4 Hz. The characteristic $^{13}C\{^1H\}$ NMR spectroscopic features of **8a** and **8b** comprise downfield resonances at δ = 179.1 and 182.2 ppm, respectively, assignable to the vinyl C-α atom. In the absence of MeOH these reactions give the simple substitution products **5a** and **5b**, respectively. The reaction proceeds with substitution as the first step, followed by opening of the cyclopropenyl ring by MeOH to give the vinylidene ligand. This was confirmed by a separate experiment where **5** was allowed to react with MeOH, resulting in protonation followed by a nucleophilic attack of methoxide at C-α of the vinylidene ligand to give the final product. In our previous paper we reported that MeOH is able to open three-membered rings in some cases.[6]

Concluding Remark

The (cyclopropenyl)ruthenium complex **4a**, containing a Tp ligand, has been prepared by deprotonation of the vinylidene precursor **3a**. No deprotonation was observed in the reaction of **3b**−**3e** with NaOMe or nBu_4NOH which may be attributed to the reduced cationic character of vinylidene complexes caused by the presence of the Tp ligand. Unlike its Cp analogue, complex **4a** undergoes a facile phosphane substitution reaction with several two-electron donor molecules. This property was taken advantage of to prepare novel complexes of Ru. For example, *n*BuNC readily displaces one of the phosphane ligands of **4a** to give a mixture of diastereomers **5** in a 4:1 ratio. Reaction of **4a** with *n*BuNC in the presence of MeOH gives the vinyl ether product **8a**, which results from a displacement reaction followed by nucleophilic addition of the MeO^- group at C-α.

Experiment Section

General Procedures: All manipulations were performed under nitrogen using vacuum-line, drybox, and standard Schlenk techniques. CH_3CN and CH_2Cl_2 were distilled from CaH_2 and diethyl ether and THF from Na/benzophenone ketyl. All other solvents and reagents were of reagent grade and were used without further purification. NMR spectra were recorded with Bruker AC-200 and AM-300WB FT NMR spectrometers at room temperature (unless stated otherwise) and are reported in δ units with residual protons in the solvent as an internal standard [$CDCl_3$: δ = 7.24 ppm; CD_3CN: δ = 1.93 ppm; $CD_3C(O)CD_3$: δ = 2.04 ppm]. FAB mass spectra were recorded with a JEOL SX-102A mass spectrometer. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instrument at the National Taiwan University. The complexes [$RuCl_2(PPh_3)_3$][20] and **4a**[6] were prepared according to literature methods.

Synthesis of [$RuCl_2(C_3H_3NNH)_2(PPh_3)_2$] (1): Pyrazole (0.38 g, 5.60 mmol) was added to a solution of [$RuCl_2(PPh_3)_3$] (2.45 g,

2.80 mmol) in 20 mL of THF, and the reaction mixture was heated to 60 °C for 1 h. After cooling and removal of the solvent under reduced pressure, the residue was dissolved in CH_2Cl_2. Addition of hexane afforded a bright yellow precipitate, which was filtered off, washed with hexane and dried under vacuum to give **1** (2.12 g, 91% yield). ^{1}H NMR ($CDCl_3$): δ = 5.91 (t, $J_{H,H}$ = 2.3 Hz, 3 H, Tp), 7.32−6.91 (m, Ph, Tp), 8.09 (d, $J_{H,H}$ = 2.1 Hz, 3 H, Tp), 11.67 (s, 2 H, NH) ppm. ^{31}P NMR ($CDCl_3$): δ = 40.8 ppm. MS (FAB): *m*/*z* = 832.1 [M^+], 764.2 [M^+ − HPz], 502.2 [M^+ − HPz − PPh_3]. $C_{42}H_{38}BCl_2N_4P_2Ru$ (832.68): calcd. C 60.58, H 4.60, N 6.73; found C 60.46, H 4.54, N 6.65.

Preparation of [Ru(C≡C−Ph)(Tp)(PPh$_3$)$_2$] (2): An excess of phenylacetylene (4.17 mL, 36.1 mmol) and NEt_3 (6.3 mL, 36.1 mmol) were added to 50 mL of an MeOH solution of **1** (3.00 g, 3.61 mmol), and the solution was heated to reflux for 90 min. The yellow precipitate thus formed was filtered off and washed with MeOH and hexane. The product was dried under vacuum and was subsequently identified as compound **2** (3.43 g, 97% yield). Yellow crystals of **2** were obtained by slow diffusion of hexane into a $CHCl_3$ solution of **2** at room temperature. ^{1}H NMR ($CDCl_3$): δ = 5.20 (d, $J_{H,H}$ = 1.8 Hz, 1 H, Tp), 5.31 (t, $J_{H,H}$ = 2.1 Hz, 1 H, Tp), 5.54 (t, $J_{H,H}$ = 2.3 Hz, 2 H, Tp), 7.24−6.91 (m, Ph, Tp), 7.40 (d, $J_{H,H}$ = 2.0 Hz, 2 H, Tp), 7.58 (d, $J_{H,H}$ = 2.1 Hz, 1 H, Tp) ppm. ^{13}C NMR [$CD_3C(O)CD_3$]: δ = 122.7 (C-β), 135.8 (t, $J_{C,P}$ = 12.3 Hz, C-α), 145.7−127.2 (Ph, Tp) ppm. ^{31}P NMR ($CDCl_3$): δ = 48.6 ppm. MS (FAB): *m*/*z* = 940.1 [M^+], 678.1 [M^+ − PPh_3], 577.1 [M^+ − PPh_3 − C_2Ph], 363.0 [M^+ − PPh_3 − C_2Ph − Tp]. $C_{53}H_{44}BN_6P_2Ru$ (938.75): calcd. C 67.81, H 4.72, N 8.95; found C 67.94, H 4.59, N 8.91.

Synthesis of [Ru{=C=C(Ph)CH$_2$(CH=CH$_2$)}(Tp)(PPh$_3$)$_2$]I (3b): $ICH_2{=}CH_2$ (0.46 mL, 3.5 mmol) was added to a Schlenk flask charged with complex **2** (1.41 g, 1.50 mmol) in 50 mL of CH_2Cl_2. The clear solution was stirred for 16 h and then the volume of solvent was reduced to about 5 mL. This mixture was slowly added to 90 mL of vigorously stirred diethyl ether. The green precipitate thus formed was filtered off and washed with diethyl ether and hexane to give compound **3b** (1.33 g, 77%). ^{1}H NMR ($CDCl_3$): δ = 3.05 (d, $J_{H,H}$ = 5.5 Hz, 2 H, CH_2), 4.95 (dd, $J_{H,H}$ = 15.3, 2.7 Hz, 1 H, =CH), 5.05 (dd, $J_{H,H}$ = 10.3, 2.7 Hz, 1 H, =CH), 5.38 (d, $J_{H,H}$ = 1.9 Hz, 1 H, Tp), 5.53 (m, 1 H, CH=), 5.56 (t, $J_{H,H}$ = 1.9 Hz 1 H, Tp), 5.61 (t, $J_{H,H}$ = 2.1 Hz, 2 H, Tp), 6.59−7.42 (m, Ph), 7.57 (d, $J_{H,H}$ = 2.2 Hz, 2 H, Tp), 7.84 (d, $J_{H,H}$ = 1.9 Hz 1 H, Tp) ppm. ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_2), 105.8 (=CH_2), 118.4 (C-β), 105.9−146.2 (m, Ph, Tp), 153.8 (=CH), 377.5 (t, $J_{C,P}$ = 16.3 Hz, C-α) ppm. ^{31}P NMR ($CDCl_3$): δ = 37.8 ppm. MS (FAB): *m*/*z* = 981.3 [M^+ − I], 719.3 [M^+ − I − PPh_3], 577.1 [M^+ − I − PPh_3 − $C_2PhCH_2CH{=}CH_2$]. $C_{56}H_{50}BIN_6P_2Ru$ (1107.7): calcd. C 60.71, H 4.55, N 7.59; found C 60.62, H 4.43, N 7.63.

[Ru{=C=C(Ph)CH$_2$CH=C(Me)$_2$}(Tp)(PPh$_3$)$_2$]Br (3c): Yield 1.36 g, in 83%; prepared in a similar manner from 1.43 g (1.52 mmol) of **2** and excess $BrCH_2CH{=}C(Me)_2$ (3.7 mmol) at room temperature. ^{1}H NMR ($CDCl_3$): δ = 1.18 (s, 3 H, Me), 1.62 (s, 3 H, Me), 3.12 (d, $J_{H,H}$ = 5.1 Hz, 2 H, CH_2), 4.90 (m, 1 H, CH=), 5.42 (t, $J_{H,H}$ = 1.9 Hz, 1 H, Tp), 5.54 (t, $J_{H,H}$ = 2.2 Hz, 2 H, Tp), 6.41 (d, $J_{H,H}$ = 2.1 Hz, 1 H, Tp), 6.45 (d, $J_{H,H}$ = 2.0 Hz, 2 H, Tp), 6.96−7.42 (m, Ph) 7.66 (d, $J_{H,H}$ = 2.0 Hz, 2 H, Tp), 7.83 (d, $J_{H,H}$ = 2.1 Hz, 1 H, Tp) ppm. ^{13}C NMR ($CDCl_3$): δ = 18.1 (CH_2), 21.2 (Me), 25.6 (Me), 118.3 (C-β), 104.3−146.5 (Ph, Tp), 379.8 (t, $J_{C,P}$ = 15.8 Hz, C-α) ppm. ^{31}P NMR ($CDCl_3$): δ = 37.9 ppm. MS (FAB): *m*/*z* = 1009.3 [M^+ − Br], 747.3 [M^+ − Br − PPh_3], 577.1 [M^+ − Br − PPh_3 − $C_2PhCH_2CH{=}CMe_2$]. $C_{58}H_{54}BBrN_6P_2Ru$ (1088.8): calcd. C 63.98, H 5.00, N 7.72; found C 63.87, H 4.91, N 7.81.

[Ru{=C=C(Ph)CH$_2$Ph}(Tp)(PPh$_3$)$_2$]I (3d): Yield 1.45 g, in 87%; prepared in a similar manner from 1.50 g (1.59 mmol) of **2** and excess $BrCH_2Ph$ (0.40 mL, 3.0 mmol) at room temperature. ^{1}H NMR ($CDCl_3$): δ = 3.90 (s, 2 H, CH_2), 5.29 (br, 1 H, Tp), 5.34 (br, 1 H, Tp), 5.39 (br, 1 H, Tp), 5.54 (t, $J_{H,H}$ = 2.0 Hz, 2 H, Tp), 7.73−6.59 (m, Ph, Tp), 7.86 (d, $J_{H,H}$ = 2.1 Hz, 1 H, Tp) ppm. ^{13}C NMR ($CDCl_3$): δ = 16.0 (CH_2), 147.3−108.4 (Ph, Tp), 378.5 (t, $J_{C,P}$ = 15.8 Hz, C-α) ppm. ^{31}P NMR ($CDCl_3$): δ = 37.4 ppm. MS (FAB): *m*/*z* = 1031.4 [M^+ − Br], 769.5 [M^+ − Br − PPh_3], 577.1 [M^+ − Br − PPh_3 − C_2PhCH_2Ph]. $C_{60}H_{52}BBrN_6P_2Ru$ (1110.8): calcd. C 64.87, H 4.72, N 7.57; found C 64.91, H 4.67, N 7.41.

Preparation of [Tp(PPh$_3$)$_2$Ru=C=C(Ph)CH$_2$COOMe]Br (3e): A mixture of complex **2** (2.80 g, 3.10 mmol) and $BrCH_2COOMe$ (0.5 mL, 5.10 mmol) in 40 mL of CH_2Cl_2/CH_3Cl (3:1) was heated to reflux for 6 h. The workup procedure was the same as that for **3d**. Purification by recrystallization from CH_2Cl_2/hexane (1:5) gave **3e** (1.45 g, 87% yield). ^{1}H NMR ($CDCl_3$): δ = 3.10 (s, 2 H, CH_2), 3.59 (s, 3 H, OMe), 5.45 (br, 1 H, Tp), 5.53 (br, 1 H, Tp), 5.61 (br, 1 H, Tp), 5.77 (t, $J_{H,H}$ = 2.0 Hz, 2 H, Tp), 6.32 (br, 2 H, Tp), 7.57−6.59 (m, Ph, Tp), 7.65 (d, $J_{H,H}$ = 1.9 Hz, 2 H, Tp), 7.79 (d, $J_{H,H}$ = 2.0 Hz, 1 H, Tp) ppm. ^{13}C NMR ($CDCl_3$): δ = 19.1 (CH_2), 57.1 (CH_3), 106.4−145.6 (Ph, Tp), 171.4 (COO), 378.5 (t, $J_{C,P}$ = 15.6 Hz, C-α) ppm. ^{31}P NMR ($CDCl_3$): δ = 38.4 ppm. MS (FAB): *m*/*z* = 1013.3 [M^+ − Br], 751.2 [M^+ − Br − PPh_3], 577.4 [M^+ − Br − PPh_3 − C_2PhCH_2COOMe]. $C_{56}H_{50}BBrN_6O_2P_2Ru$ (1092.7): calcd. C 61.55, H 4.61, N 7.69; found C 61.61, H 4.51, N 7.82.

Synthesis of 5a: Complex **4a** (0.50 g, 0.51 mmol) was dissolved in CH_2Cl_2 (20 mL), and *n*BuNC (0.05 mL, 0.51 mmol) was added. The mixture was stirred for 50 min to afford a bright-yellow solution. The solvent was then removed under vacuum and the solid residue was extracted with 20 mL of diethyl ether. The extract was filtered through Celite, and the filtrate was dried to give a bright-yellow solid, which was washed with hexane (2 × 10 mL), and dried under vacuum to give a mixture of diastereoisomers of **5a** (0.327 g, 80.3% yield). ^{1}H NMR [$CD_3C(O)CD_3$]: major isomer: δ = 0.75 (t, $J_{H,H}$ = 7.5 Hz, 3 H, CH_3), 0.93 (s, 1 H, C*H*), 1.23 (m, 2 H, CH_2), 1.53 (m, 2 H, CH_2), 3.72 (t, $J_{H,H}$ = 6.6 Hz, 2 H, CH_2), 5.88 (t, $J_{H,H}$ = 2.2 Hz, 1 H, Tp), 5.96 (t, $J_{H,H}$ = 2.1 Hz, 1 H, Tp), 6.01 (t, $J_{H,H}$ = 1.8 Hz, 1 H, Tp), 6.76 (br, 1 H, Tp), 6.78 (br, 1 H, Tp), 6.86 (br, 1 H, Tp), 7.69 (d, $J_{H,H}$ = 2.0 Hz, 1 H, Tp), 7.07−7.40 (m, Ph), 7.81 (d, $J_{H,H}$ = 2.0 Hz, 1 H, Tp), 7.88 (d, $J_{H,H}$ = 2.1 Hz, 1 H, Tp) ppm; minor isomer: δ = 0.77 (t, $J_{H,H}$ = 7.4 Hz, 3 H, CH_3), 1.16 (s, 1 H, C*H*CN), 1.26 (m, 2 H, CH_2), 1.55 (m, 2 H, CH_2), 3.84 (t, $J_{H,H}$ = 6.7 Hz, 2 H, CH_2), 6.14 (t, $J_{H,H}$ = 2.2 Hz, 1 H, Tp), 6.21 (t, $J_{H,H}$ = 2.1 Hz, 1 H, Tp), 6.34 (t, $J_{H,H}$ = 2.0 Hz, 1 H, Tp), 6.76 (br, 1 H, Tp), 6.94 (br, 2 H, Tp), 7.40 −7.07 (m, Ph), 7.71 (d, $J_{H,H}$ = 2.1 Hz, 1 H, Tp), 7.92 (d, $J_{H,H}$ = 1.9 Hz, 1 H, Tp), 8.12 (d, $J_{H,H}$ = 2.0 Hz, 1 H, Tp) ppm. ^{13}C NMR [$CD_3C(O)CD_3$]: major isomer: δ = 3.8 (CH), 13.5 (*C*H_3), 20.2 (*C*H_2), 32.3 (*C*H_2), 44.8 (*C*H_2), 116.3 (CN), 128.7 (d, $J_{C,P}$ = 11.6 Hz, C-α), 146.9 −129.3 (Ph, Tp), 160.1 (d, $J_{C,P}$ = 22.5 Hz, *C*N) ppm; minor isomer: δ = 3.5 (CH), 13.5 (*C*H_3), 20.2 (*C*H_2), 32.2 (*C*H_2), 44.7 (*C*H_2), 115.2 (CN), 128.8 (d, $J_{C,P}$ = 11.6 Hz, C-α), 129.3−146.9 (Ph, Tp), 163.2 (d, $J_{C,P}$ = 21.3 Hz, *C*N) ppm. ^{31}P NMR [$CD_3C(O)CD_3$]: δ = 54.1, 52.7 (4:1) ppm. MS (FAB): *m*/*z* = 800.3 [M^+], 660.3 [M^+ − $C_2PhCHCN$], 577.2 [M^+ − $C_2PhCHCN$ − *n*BuNC]. $C_{42}H_{40}BN_8PRu$ (799.65): calcd. C 63.08, H 5.04, N 14.01; found C 62.98, H 4.96, N 13.89.

Synthesis of 5b: Complex **4a** (1.01 g, 1.03 mmol) was dissolved in CH_2Cl_2 (30 mL), and *t*BuNC (0.11 mL, 1.03 mmol) was added.

The mixture was stirred at room temperature to afford a bright-yellow solution. The solvent was then removed under vacuum, and the solid residue was extracted with 20 mL of diethyl ether. The extract was filtered, and the filtrate was dried to give a bright-yellow solid, which was washed with hexane (2 × 10 mL) and dried under vacuum to give a diastereomeric mixture of **5b** (0.62 g, 79.1% yield). ^{1}H NMR [$CD_3C(O)CD_3$]: major isomer: δ = 0.96 (s, 1 H, C*H*), 1.47 (s, 9 H, Me), 5.81 (t, $J_{H,H}$ = 2.1 Hz, 1 H, Tp), 5.97 (t, $J_{H,H}$ = 2.1 Hz, 1 H, Tp), 6.11 (t, $J_{H,H}$ = 1.9 Hz, 1 H, Tp), 6.71 (br, 1 H, Tp), 6.74 (br, 1 H, Tp), 6.83 (br, 1 H, Tp), 7.46 −7.07 (m, Ph), 7.73 (d, $J_{H,H}$ = 2.1 Hz, 1 H, Tp), 7.80 (d, $J_{H,H}$ = 2.2 Hz, 1 H, Tp), 7.82 (d, $J_{H,H}$ = 2.0 Hz, 1 H, Tp) ppm; minor isomer: δ = 1.08 (s, 1 H, C*H*), 1.48 (s, 9 H, Me), 6.13 (t, $J_{H,H}$ = 2.1 Hz, 1 H, Tp), 6.20 (t, $J_{H,H}$ = 2.0 Hz, 1 H, Tp), 6.32 (t, $J_{H,H}$ = 2.2 Hz, 1 H, Tp), 6.72 (br, 1 H, Tp), 6.99 (br, 2 H, Tp), 7.42−7.17 (m, Ph), 7.67 (d, $J_{H,H}$ = 2.0 Hz, 1 H, Tp), 7.92 (d, $J_{H,H}$ = 2.1 Hz, 1 H, Tp),8.11 (d, $J_{H,H}$ = 2.0 Hz, 1 H, Tp) ppm. ^{13}C NMR [$CD_3C(O)CD_3$]: major isomer: δ = 3.8 (CH), 32.1 (C*Me*$_3$), 58.7 (*C*Me$_3$), 119.2 (CN), 126.5 (d, $J_{C,P}$ = 12.1 Hz, C-α), 141.9 −129.3 (Ph, Tp), 163.4 (d, $J_{C,P}$ = 21.4 Hz, *C*N) ppm; minor isomer: δ = 3.5 (CH), 31.2 (*Me*$_3$), 55.3 (*C*Me$_3$), 118.9 (CN), 127.1 (d, $J_{C,P}$ = 11.2 Hz, C-α), 129.3−146.9 (Ph, Tp), 164.1 (d, $J_{C,P}$ = 20.1 Hz, *C*N) ppm. ^{31}P NMR [$CD_3C(O)CD_3$]: δ = 52.9, 53.9 (4:1) ppm. MS (FAB): *m*/*z* = 801.1 [M$^+$ + 1], 660.3 [M$^+$ − C_2PhCHCN], 577.2 [M$^+$ − C_2PhCHCN − *t*BuNC]. $C_{42}H_{40}BN_8PRu$ (799.65): calcd. C 63.08, H 5.04, N 14.01; found C 63.12, H 5.10, N 13.97.

Synthesis of 5c: An excess of PhCN (0.21 mL, 2.02 mmol) was added to a solution of **4a** (1.00 g, 1.02 mmol) in 20 mL of CH_2Cl_2. The solution was stirred at room temperature (the color changed from yellow to brown) and then the solvent was removed under vacuum. The solid residue was extracted with diethyl ether, and the extract was filtered. The volume of the resulting solution was reduced to 5 mL and 40 mL of hexane was added to form an orange precipitate, which was filtered and washed twice with 10 mL of hexane. The product was dried under vacuum (0.60 g, 72% yield). ^{1}H NMR [$CD_3C(O)CD_3$]: major isomer: δ = 1.13 (s, 1 H, C*H*CN), 5.90 (t, $J_{H,H}$ = 2.0 Hz, 1 H, Tp), 6.02 (t, $J_{H,H}$ = 2.1 Hz, 1 H, Tp), 6.06 (br, 1 H, Tp), 6.78 (br, 1 H, Tp), 6.97 (br, 1 H, Tp), 7.69−7.03 (m, Ph),7.91 (d, $J_{H,H}$ = 2.2 Hz, 2 H, Tp) ppm; minor isomer: δ = 0.79 (s, 1 H, C*H*), 5.92 (t, $J_{H,H}$ = 2.1 Hz, 1 H, Tp), 6.01 (t, $J_{H,H}$ = 1.9 Hz, 1 H, Tp), 6.05 (d, $J_{H,H}$ = 2.0 Hz, 2 H, Tp), 6.43 (d, $J_{H,H}$ = 1.9 Hz, 2 H, Tp), 6.96 (d, $J_{H,H}$ = 2.1 Hz, 2 H, Tp), 7.64 −7.01 (m, Ph), 7.93 (d, $J_{H,H}$ = 2.0 Hz, 2 H, Tp) ppm. ^{13}C NMR [$CD_3C(O)CD_3$] major isomer: δ = 4.1 (CH), 116.1 (NCPh), 119.2 (CN), 132.6 (d, $J_{C,P}$ = 12.3 Hz, C-α), 147.9 −123.1 (Ph, Tp) ppm. ^{31}P NMR [$CD_3C(O)CD_3$]: δ = 54.5, 54.8 (4:1) ppm. MS (FAB): *m*/*z* = 821.4 [M$^+$ + 1], 718.4 [M$^+$ + 1 − PhCN], 577.1 [M$^+$ + 1 − PhCN − C_2PhCHCN]. $C_{44}H_{36}BN_8PRu$ (819.64): calcd. C 64.47, H 4.43, N 13.69; found C 64.49, H 4.44, N 13.63.

Synthesis of 5d: An excess of $CF_3C_6H_4CN$ (0.14 mL, 2.04 mmol) was added to a solution of **4a** (1.00 g, 1.02 mmol) in 20 mL of CH_2Cl_2. The solution was stirred for 50 min (the color changed from yellow to brown) and then the solvent was removed under vacuum. The solid residue was extracted with diethyl ether, and the extract was filtered. The volume of the resulting solution was reduced to 5 mL and 40 mL of hexane was added to form a orange precipitate, which was filtered and washed twice with 10 mL of hexane. The product was dried under vacuum (0.70 g, 77% yield). ^{1}H NMR [$CD_3C(O)CD_3$] major isomer: δ = 1.08 (s, 1 H, C*H*), 5.85 (t, $J_{H,H}$ = 2.2 Hz, 1 H, Tp), 5.98 (t, $J_{H,H}$ = 2.1 Hz, 1 H, Tp), 6.02 (t, $J_{H,H}$ = 1.8 Hz, 1 H, Tp), 6.76 (br, 1 H, Tp), 6.78 (br, 1 H, Tp), 6.86 (br, 1 H, Tp), 7.07−7.40 (m, Ph), 7.69 (d, $J_{H,H}$ = 2.0 Hz, 1 H, Tp), 7.81 (d, $J_{H,H}$ = 2.2 Hz, 1 H, Tp), 7.85 (d, $J_{H,H}$ = 2.2 Hz, 1 H, Tp) ppm; minor isomer: δ = 0.82 (s, 1 H, C*H*), 5.91 (t, $J_{H,H}$ = 2.0 Hz, 1 H, Tp), 6.05 (t, $J_{H,H}$ = 1.9 Hz, 1 H, Tp), 6.07 (d, $J_{H,H}$ = 2.1 Hz, 2 H, Tp), 6.46 (d, $J_{H,H}$ = 2.0 Hz, 2 H, Tp), 6.89 (d, $J_{H,H}$ = 2.0 Hz, 2 H, Tp), 7.01−7.64 (m, Ph), 7.97 (d, $J_{H,H}$ = 2.1 Hz, 2 H, Tp) ppm. ^{13}C NMR [$CD_3C(O)CD_3$]: major isomer: δ = 5.1 (CH), 110.6 (q, $J_{C,F}$ = 282.0 Hz, *C*F$_3$), 111.2 (NCPh), 118.1 (CN), 131.7 (d, $J_{C,P}$ = 11.9 Hz, C-α), 148.2−126.6 (Ph, Tp) ppm. ^{31}P NMR [$CD_3C(O)CD_3$]: δ = 53.6, 54.3 (4:1) ppm. MS (FAB): *m*/*z* = 888.4 [M$^+$ + 1], 718.4 [M$^+$ + 1 − $CF_3C_6H_4CN$], 577.1 [M$^+$ + 1 − $CF_3C_6H_4CN$ − C_2PhCHCN]. $C_{45}H_{35}BF_3N_8PRu$ (887.63): calcd. C 60.88, H 3.97, N 12.62; found C 60.78, H 4.08, N 12.51.

Synthesis of [Ru{=C=C(Ph)CH(I)CN}(Tp)(PPh$_3$)$_2$]I (6): CH_2Cl_2 (30 mL) was added to a solid mixture of **4a** (0.51 g, 0.52 mmol) and I_2 (0.13 g, 0.52 mmol) at 0 °C. The mixture was stirred for 2 min whereupon the color changed from yellow to green; the solvent was then removed under vacuum. The residual solid was extracted twice with 20 mL of diethyl ether and, after filtration, the solvent was removed under vacuum to give complex **6** (0.45 g, 69% yield). ^{1}H NMR [$CD_3C(O)CD_3$]: δ = 3.23 (s, 1 H, C*H*), 5.43 (t, $J_{H,H}$ = 2.1 Hz, 1 H, Tp), 5.55 (t, $J_{H,H}$ = 2.0 Hz, 1 H, Tp), 5.76 (d, $J_{H,H}$ = 2.0 Hz, 1 H, Tp), 5.65 (d, $J_{H,H}$ = 2.1 Hz, 1 H, Tp), 6.79 (d, $J_{H,H}$ = 1.9 Hz 1 H, Tp), 7.56−7.11 (m, Tp, Ph), 7.73 (m, 2 H, Tp), 7.98 (d, $J_{H,H}$ = 2.1 Hz, 1 H, Tp) ppm. ^{13}C NMR ($CDCl_3$): δ = 26.1 (CH), 119.4 (CN), 106.8−147.2 (Ph, Tp, C-β), 374.5 (t, $J_{C,P}$ = 15.1 Hz, C-α) ppm. ^{31}P NMR [$CD_3C(O)CD_3$]: δ = 33.6, 34.3 (AB, $J_{P,P}$ = 26.9 Hz) ppm. MS (FAB): *m*/*z* = 1107.1 [M$^+$ − I], 980.3 [M$^+$ − 2I], 839.2 [M$^+$ − 2 I − C_2PhCHCN], 577.1 [M$^+$ − 2 I − C_2PhCHCN − PPh_3]. $C_{55}H_{47}BI_2N_7P_2Ru$ (1233.6): calcd. C 53.55, H 3.84, N 7.95; found C 53.46, H 4.01, N 8.03.

Synthesis of [Ru{=C=C(Ph)CH(I)CN}(Tp)(PPh$_3$)(*n*BuNC)]I (7): CH_2Cl_2 (30 mL) was added to a solid mixture of **5a** (0.17 g, 0.21 mmol) and I_2 (0.054 g, 0.17 mmol). The mixture was stirred for 5 min and the solvent was then removed under vacuum. The residual solid was extracted twice with 20 mL of diethyl ether and, after filtration, the solvent was removed under vacuum to give **7** (0.14 g, 78% yield). ^{1}H NMR [$CD_3C(O)CD_3$]: δ = 0.73 (t, $J_{H,H}$ = 7.4 Hz, 3 H, CH_3), 1.03 (m, 2 H, C*H*$_2$), 1.94 (m, 2 H, C*H*$_2$), 3.46 (t, $J_{H,H}$ = 6.2 Hz, 2 H, C*H*$_2$), 3.56 (s, 1 H, C*H*), 5.96 (t, $J_{H,H}$ = 2.3 Hz, 1 H, Tp), 6.10 (t, $J_{H,H}$ = 2.1 Hz, 1 H, Tp), 6.36 (d, $J_{H,H}$ = 2.1 Hz, 1 H, Tp), 6.43 (d, $J_{H,H}$ = 2.1 Hz, 1 H, Tp), 7.39−7.01 (m, Tp, Ph), 7.67 (d, $J_{H,H}$ = 2.1 Hz, 1 H, Tp), 7.69 (d, $J_{H,H}$ = 2.3 Hz, 1 H, Tp), 7.75 (d, $J_{H,H}$ = 2.1 Hz, 1 H, Tp) ppm. ^{13}C NMR [$CD_3C(O)CD_3$]: δ = 14.2 (*C*H$_3$), 20.0 (*C*H$_2$), 25.4 (CH), 35.2 (*C*H$_2$), 44.1 (*C*H$_2$), 126.3 (CN), 108.4−148.9 (Ph, Tp), 167.2 (d, $J_{C,P}$ = 22.9 Hz, *C*N), 367.3 (d, $J_{C,P}$ = 16.4 Hz, C-α) ppm. ^{31}P NMR [$CD_3C(O)CD_3$]: δ = 45.9 ppm. MS (FAB): *m*/*z* = 926.3 [M$^+$ − I], 800.1 [M$^+$ − 2 I], 660.2 [M$^+$ − 2 I − C_2PhCHCN], 577.2 [M$^+$ − 2 I − C_2PhCHCN − *n*BuNC]. $C_{42}H_{40}BI_2N_8PRu$ (1053.5): calcd. C 47.88, H 3.83, N 10.64; found C 47.81, H 4.02, N 10.70.

Synthesis of [Ru{C(OMe)=C(Ph)CH$_2$CN}(Tp)(PPh$_3$)(*n*BuNC)] (8a): A solution of **4a** (1.50 g, 1.53 mmol) was dissolved in methanol and *n*BuNC (0.30 mL, 3.06 mmol) was added. After stirring for 10 min, the yellow solution became bright yellow. The solution was filtered through Celite and the solvent was removed under vacuum to give **8a** (1.01 g, 85% yield). ^{1}H NMR [$CD_3C(O)CD_3$]: δ = 0.70 (t, $J_{H,H}$ = 7.5 Hz, 3 H, CH_3), 0.86 (m, 2 H, C*H*$_2$), 1.88 (m, 2 H, C*H*$_2$), 2.79 (d, $J_{H,H}$ = 16.4 Hz, 1 H, C*H*), 3.63 (t, $J_{H,H}$ = 6.4 Hz, 2 H, C*H*$_2$), 3.86 (d, $J_{H,H}$ = 16.4 Hz, 1 H, CH*H*), 5.63 (t, $J_{H,H}$ = 1.8 Hz, 1 H, Tp), 6.05 (br, 1 H, Tp), 6.11 (br, 1 H, Tp), 7.00 (br, 1 H, Tp), 7.60−7.02 (m, Ph, Tp), 7.81 (d, $J_{H,H}$ = 2.0 Hz, 1 H, Tp) ppm. ^{13}C NMR [$CD_3C(O)CD_3$]: δ = 13.5 (*C*H$_3$), 21.1 (*C*H$_2$), 22.4

(CH_2), 31.1 (CH_2), 43.1 (CH_2), 55.4 (OMe), 115.5 (CN), 123.4−147.6 (Ph), 162.1 (d, $J_{C,P}$ = 23.1 Hz, *C*N),179.1 (d, $J_{C,P}$ = 15.3 Hz, C-α) ppm. ^{31}P NMR [$CD_3C(O)CD_3$]: δ = 46.9 ppm. MS (FAB): *m*/*z* = 832.3 [M^+], 660.1 [M^+ − (OMe)C=C(Ph)(CH_2CN)], 577.1 [M^+ − (OMe)C=C(Ph)(CH_2CN) − *n*BuNC]. $C_{43}H_{44}BN_8OPRu$ (831.69): calcd. C 62.08, H 5.33, N 13.47; found C 62.16, H 5.40, N 13.35.

Synthesis of [Ru{C(OMe)=C(Ph)CH_2CN}Tp(PPh_3)(*t*BuNC)] (8b): Complex **4a** (0.5 g, 0.51 mmol) was dissolved in CH_3OH (20 mL), and *t*BuNC (0.30 mL, 3.02 mmol) was added. The mixture was stirred for 50 min to afford a bright-yellow solution. The solvent was then removed under vacuum and the solid residue was extracted with diethyl ether. The extract was filtered, and the filtrate was dried under vacuum to give a bright-yellow solid, which was washed with hexane (2 × 10 mL), and dried to give **8b** (0.327 g, 80.3% yield). ^1H NMR [$CD_3C(O)CD_3$]: δ = 1.44 (s, 9 H, C*Me*$_3$), 2.84, 3.87 (2d, $J_{H,H}$ = 15.3 Hz, 1 H, CH_2CN), 5.61 (br, 1 H, Tp), 6.15 (br, 1 H, Tp), 6.21 (br, 1 H, Tp), 6.43 (br, 1 H, Tp), 6.96−7.56 (m, Ph, Tp), 7.78 (d, $J_{H,H}$ = 2.2 Hz, 1 H, Tp) ppm. ^{13}C NMR [$CD_3C(O)CD_3$]: δ = 32.7 (C*Me*$_3$), 55.4 (OMe), 113.2 (CN), 123.4−147.6 (Ph), 182.2 (d, $J_{C,P}$ = 16.1 Hz, C-α) ppm. ^{31}P NMR [$CD_3C(O)CD_3$]: δ = 46.8 ppm. MS (FAB): *m*/*z* = 832.2 [M^+], 660.1 [M^+ − (OMe)C=C(Ph)(CH_2CN)], 577.1 [M^+ − (OMe)C=C(Ph)(CH_2CN) − *t*BuNC]. $C_{43}H_{44}BN_8OPRu$ (831.69): calcd. C 62.08, H 5.33, N 13.47; found C 62.11, H 5.34, N 13.51.

X-ray Diffraction Analysis: Dark-yellow crystals of **1** suitable for an X-ray diffraction study were grown directly from CH_2Cl_2. A suitable single crystal of dimensions 0.10 × 0.40 × 0.50 mm was glued to a glass fiber and mounted on a Nonius CD4 diffractometer. The data were collected using Mo-K_α radiation (at 298 K). The data were processed and the structure was solved and refined with the SHELXTL program. The structure was solved by direct methods and confirmed by Patterson methods. Hydrogen atoms were placed geometrically using the riding model with thermal parameters set to 1.2-times that of the atom to which they are attached (1.5-times for the methyl hydrogen atoms). Yellow crystals of **2** suitable for an X-ray diffraction study were obtained as above. A suitable single crystal of dimensions 0.05 × 0.10 × 0.15 mm was mounted on a SMART CCD diffractometer. The data were collected using 3-kW sealed-tube Mo-K_α radiation (at 298 K). The exposure time was 5 s per frame. SADABS (Siemens area detector absorption) absorption correction was applied, and decay was negligible. Data were processed with the SHELXTL program.[21] The structure was solved by direct methods refining on intensities of all data. Hydrogen atoms were placed geometrically using the riding model. Crystal data for **1** and **2** are listed in Table 1.

Table 1. Crystal data and structure refinement for **1** and **2**

	1	**2**
Empirical formula	$C_{42}H_{38}Cl_2N_4P_2Ru$ CH_2Cl_2	$C_{53}H_{45}BN_6P_2Ru$
Formula mass	917.64	939.77
T [K]	295(2)	296(2)
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	9.827(3)	10.277(2)
b [Å]	13.163(3)	11.930(3)
c [Å]	17.0307(20)	20.164(6)
α [°]	81.404(13)	93.57(2)
β [°]	78.311(16)	99.82(2)
γ [°]	78.289(19)	111.54(2)
V [Å^3]	2098.9(7)	2244.6(10)
Z	2	2
ρ(calcd.) [Mg/m^3]	1.452	1.390
F(000)	935	968
GOF	1.50	0.929
*R*1, *wR*2 [$I > 2\sigma(I)$][a]	0.048, 0.042	0.0491, 0.1195
(all data)	0.0888, 0.1417	0.0830, 0.1480

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

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