Synthesis and Reactivity of the Ruthenium Cyclopropenyl Complex with a Tp Ligand

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Treatment of $\text{Tp}(\text{PPh}_3)_2\text{Ru}-\text{C}\equiv\text{C}-\text{Ph}$ (**1**) with ICH_2CN affords the cationic vinylidene complex $[\text{Tp}(\text{PPh}_3)_2\text{Ru}=\text{C}=\text{C}(\text{Ph})\text{CH}_2\text{CN}]\text{I}$ (**2**). The neutral ruthenium cyclopropenyl complex $\text{Tp}(\text{PPh}_3)_2\text{RuC}=\text{C}(\text{Ph})\text{CHCN}$ (**3**) is then prepared by deprotonation of **2**. Facile displacement of one phosphine ligand of **3** by CH_3CN yields a diastereomeric mixture in a 4:1 ratio of the substitution product, $\text{Tp}(\text{PPh}_3)(\text{CH}_3\text{CN})\text{RuC}=\text{C}(\text{Ph})\text{CHCN}$ (**4**). The cyclopropenyl ring in **3** and **4** is susceptible to ring opening by electrophiles such as CF_3COOH , Ph_3CPF_6 , and HgCl_2 . The substitution reaction of **3** with pyrazole is followed by an intramolecular nucleophilic addition of the nitrogen atom at the α -carbon atom to afford the metallacyclic complex, $\text{Tp}(\text{PPh}_3)\text{Ru}(\text{C}_3\text{H}_3\text{NN})\text{C}=\text{C}(\text{Ph})\text{CH}_2\text{CN}$ (**8a**). The reaction of **3** with CO in the presence of MeOH gives $\text{Tp}(\text{PPh}_3)(\text{CO})\text{RuC}(\text{OMe})=\text{C}(\text{Ph})\text{CH}_2\text{CN}$ (**9**). The reaction of CF_3COOH with **9** yields $\text{Tp}(\text{PPh}_3)(\text{CO})\text{RuC}(\text{O})\text{CH}(\text{Ph})\text{CH}_2\text{CN}$ (**11**). The structures of **8a** and **11** have been determined by X-ray diffraction analysis.

Introduction

Transition-metal cyclopropenyl and vinylidene complexes have been the focus of many recent investigations. Organic cyclopropene is a highly strained cycloalkene with an estimated strain energy of more than 50 kcal/mol.¹ This molecule has played a crucial role in the development of an important concept of aromaticity, and its chemical reactivity has been extensively explored.² Interest in metal vinylidene complexes stems from their potential as reactive intermediates in organic and organometallic synthesis, as well as their application in catalytic processes.³ A key characteristic of vinylidene complexes appears to be the electrophilicity of the α -carbon, which adds, often easily, amines,⁴ alcohols,^{5–7} phosphines,⁸ and even fluoride.⁵ We recently

reported facile synthesis of several ruthenium cyclopropenyl complexes by deprotonation of cationic vinylidene complexes. 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, plays a role in enhancing the acidity of the proton next to the CN group. Thus the base successfully effects an intramolecular cycloaddition leading to formation of a neutral cyclopropenyl complex. We in fact found the facile cyclopropenation reaction of several ruthenium vinylidene complexes containing the cyclopentadienyl ligand. Therefore we thought a similar complex containing a tris(pyrazol-1-yl)borate ligand (Tp , $\text{B}(\text{C}_3\text{H}_3\text{N}_2)_3$) would be a suitable candidate for further investigating chemical reactivity of the ruthenium cyclopropenyl complex. In the literature, research into the coordination chemistry of the Tp ligand has mostly focused on the first-row transition metals and group VI.⁹ The chemistry of Tp complexes of the second- and third-transition series and in particular that of group VIII¹⁰ remains less developed, although there is no obvious reason this should be the case. Herein, we report preparation of two neutral tris(pyrazol-1-yl)borato ruthenium cyclopropenyl complexes: $\text{Tp}(\text{PPh}_3)_2\text{Ru}-\text{C}=\text{C}(\text{Ph})\text{CHCN}$ (**3**) and $\text{Tp}(\text{PPh}_3)(\text{CH}_3\text{CN})\text{RuC}=\text{C}(\text{Ph})\text{CHCN}$ (**4**). Electrophilic addition to these ruthenium cyclopropenyl complexes affords new vinylidene complexes. Reaction of **3** with pyrazole gives the metallacycle product, while in the presence of MeOH, reaction

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of **3** with CO gives the vinyl ether product. The mechanism of these reactions is also reported.

Results and Discussion

Tp Metal Vinylidene Complex and Its Deprotonation/Cyclopropenation. Treatment of the acetylide complex $Tp(PPh_3)_2Ru-C\equiv C-Ph$ (**1**) with ICH_2CN affords the cationic vinylidene complex $[Tp(PPh_3)_2Ru=C=C(Ph)CH_2CN]I$ (**2**) with 90% yield. Complex **2** is soluble in CH_2Cl_2 . Characteristic spectroscopic data of **2** consist of a strongly deshielded $C\alpha$ resonance as a triplet at δ 375.3 with $J_{P-C} = 16.5$ Hz in the ^{13}C NMR spectrum and a singlet ^{31}P NMR resonance at δ 36.5 in $CDCl_3$ at room temperature, which is due to fluxional behavior of the vinylidene ligand.¹¹ For comparison, the Cp ($Cp = \eta^5-C_5H_5$) analogue displayed a triplet $C\alpha$ resonance at δ 345.6 with $J_{P-C} = 17.9$ Hz in the ^{13}C NMR spectrum and a singlet ^{31}P NMR resonance at δ 42.4.

The ruthenium cyclopropenyl complex $Tp(PPh_3)_2Ru-C\equiv C(Ph)CHCN$ (**3**) can be readily prepared by deprotonation of **2** with high yield. This reaction should be carried out at 0 °C in CH_2Cl_2 since complex **3** is thermally unstable. MeONa in MeOH is found to be a better deprotonation reagent (Scheme 1) even though reaction of **2** with $n-Bu_4NF$ (1 M in THF) or DBU (1,8-diazabicyclo[5.4.0]undecene) or KOH (dissolved in a minimum amount of H_2O) also yields **3**. Complex **3** is soluble in CH_2Cl_2 , THF, and ether, but is insoluble in hexane. The diastereotopic center generated by this cyclopropenation reaction causes the two phosphine ligands to be nonequivalent. Thus, in the ^{31}P NMR spectrum of **3**, two doublet resonances at δ 48.8 and 48.1 with $J_{P-P} = 29.9$ Hz are observed. In the 1H NMR spectrum of **3**, the singlet resonance at δ 1.18 is assigned to the CHCN group of the three-membered ring. The resonance of the same group in the Cp analogue appears at δ 1.40. Facile deprotonation indicates the acidic nature of the methylene protons of **2**, which may be

ascribed to the combined effect of the cationic character and the presence of the electron-withdrawing CN substituent of the vinylidene complex.⁵ Complex **3** decomposes in $CDCl_3$ at room temperature, producing the vinylidene complex $[Tp(PPh_3)_2Ru=C=C(Ph)CH_2CN]Cl$. The proton is believed to come from trace water in the solvent.

Facile Ligand Displacement of 3. We previously reported the analogous Cp complex of **3**, which is stable with respect to the ligand substitution reaction; that is, the phosphine ligand bonds strongly to the ruthenium center, making the coordination site unavailable for an incoming substrate. In contrast, the Tp complex **3** is susceptible to ligand substitution reaction under relatively mild conditions. For example, treatment of **3** with CH_3CN at room temperature affords the air-stable ruthenium cyclopropenyl complex $Tp(PPh_3)(CH_3CN)-$

$Ru-C\equiv C(Ph)CHCN$ (**4**) with high yield. Complex **4** is stable in ether, THF, and CH_3CN , but decomposes in $CDCl_3$ to produce a complicated mixture. Complex **4**, prepared from **3**, contains two diastereomers in a 4:1 ratio, and interestingly, the major one is stable and the minor one decomposes to some unidentifiable product. The 1H NMR resonances attributed to the CHCN of the three-membered rings of the major and the minor products appear at δ 1.08 and 1.20, respectively. In the $^{13}C\{^1H\}$ NMR spectrum, the singlet resonance at δ 2.9 and the doublet resonance at δ 137.9 with $^2J_{P-C} = 11.4$ Hz are assigned to the CHN and the ruthenium-bonded $C\alpha$ carbon of the major complex, respectively. The ^{13}C NMR spectrum of the minor product was not obtained because of its low stability.

Opening of the Three-Membered Ring by Electrophiles. Treatment of **3** with CF_3COOH affords **2**, indicating the basic character of the methyne carbon of the three-membered ring. No alkylation is observed when **3** is treated with CH_3I , CH_3CH_2I , $CH_2=CHCH_2Br$, $CH\equiv C-CH_2Br$, and ICH_2CN , but treatment of **3** with trityl hexafluorophosphate at 0 °C for 20 min affords the cationic vinylidene complex $[Tp(PPh_3)_2Ru=C=C(Ph)CH(CPh_3)CN]PF_6$ (**5**) with 69% yield (Scheme 1). There are a few examples in the literature in which electrophilic addition of CPh_3^+ resulted in

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Scheme 2

formation of a C–C bond,¹⁵ even though CPh_3^+ is usually considered a hydride abstractor. Treatment of **3** with HgCl_2 similarly affords the addition product, $[\text{Tp}(\text{PPh}_3)_2\text{Ru}=\text{C}=\text{C}(\text{Ph})\text{CH}(\text{HgCl})\text{CN}]\text{Cl}$ (**6**), while treatment of **4** with HgCl_2 also gives $[\text{Tp}(\text{PPh}_3)(\text{CH}_3\text{CN})\text{Ru}=\text{C}=\text{C}(\text{Ph})\text{CH}(\text{HgCl})\text{CN}]\text{Cl}$ (**7**). Interestingly, only one diastereomer is observed for **7**. Formation of these vinylidene complexes occurs by selective cleavage of the cyclopropenyl single bond near the metal center. This selectivity is similar to that reported for the asymmetrical cyclopropenes where the metal-substituted single bond was cleaved.¹⁶ Interestingly, reaction of MeONa with **6** gives the cyclopropenyl complex **3**, and the reaction with **7** gives **4**, but no reaction was observed in the reaction of **5** with MeONa , which may be attributed to the steric effect of the trityl cation.⁵

Reaction of 3 with Pyrazole and 3,5-Dimethylpyrazole. The reaction of **3** with pyrazole in CH_2Cl_2 at room temperature did not yield the expected neutral substituted cyclopropenyl complex, but instead gave the metallacyclic complex $\text{Tp}(\text{PPh}_3)\text{Ru}-(\text{C}_3\text{H}_3\text{NN})\text{C}=\text{C}(\text{Ph})\text{CH}_2\text{CN}$ (**8a**) (Scheme 2). An intermediate **A** was observed in the initial stage of the reaction monitored by spectroscopic methods. The ^1H NMR spectrum of **A** shows two doublet resonances at δ 4.40 and 4.11 with $J_{\text{H-H}} = 18.4$ Hz assignable to gem-protons of the CH_2CN group. In the ^{31}P NMR spectrum, the singlet resonance at δ 36.7 is assigned to the zwitterionic vinylidene complex **A**. We thus believe that the reaction first causes substitution of a phosphine ligand by a pyrazole molecule, followed by protonation to open the

three-membered ring to give the intermediate **A**. This is followed by nucleophilic addition of the neighboring nitrogen atom of the pyrazole group to $\text{C}\alpha$ of **A** to give the metallacyclic complex **8a** (Scheme 2). Complex **8a** is thermally robust and stable both in solution and in solid state. The ^1H NMR spectrum of **8a** displays two doublet resonances centered at δ 3.35 and 3.18 with a coupling constant of $J_{\text{H-H}} = 17.3$ Hz assignable to the CH_2CN group. In the ^{13}C NMR spectrum, the doublet resonance at δ 163.3 with $^2J_{\text{P-C}} = 12.3$ Hz is assigned to the vinyl $\text{C}\alpha$. Reaction with 3,5-dimethylpyrazole gives a similar product, $\text{Tp}(\text{PPh}_3)\text{Ru}(\text{Me}_2\text{C}_3\text{HNN})\text{C}=\text{C}(\text{Ph})\text{CH}_2\text{CN}$ (**8b**), in lower yield, which may be attributed to the steric effect. In the ^1H NMR spectrum of **8b**, two doublet resonances at δ 3.25 and 3.17 with $J_{\text{H-H}} = 17.1$ Hz are assigned to the CH_2CN group. The doublet resonance at δ 162.2 with $^2J_{\text{P-C}} = 12.6$ Hz in the ^{13}C NMR spectrum is assigned to the vinyl $\text{C}\alpha$. A similar metallacyclic structure with a five-membered ring has also been reported recently.¹²

Structure of Metallacyclic Complex 8a. The molecular structure of **8a** has been determined by X-ray diffraction analysis (Table 1). An ORTEP diagram is shown in Figure 1, and Table 2 lists selected bond distances and angles. The structure **8a** contains two crystallographically independent Ru complexes, although there is no essential structural difference between them. The four-membered ring of **8a** is puckered. The environment about the ruthenium metal center corresponds to a slightly distorted octahedron and it is obvious that the olefin in **8a** is in an **E** configuration with the phenyl group trans to the Ru fragment, possibly because of steric reason. Three of the internal angles of the four-membered ring are $105.0(3)^\circ$, $96.7(2)^\circ$, and $93.0(2)^\circ$, while the fourth angle $\text{C}(4)-\text{Ru}(1)-\text{N}(2)$ is $65.32(14)^\circ$. The three $\text{Ru}-\text{N}(\text{Tp})$ bond lengths (2.098(3), 2.142(3), and 2.156(3) Å) are slightly longer than the average distance of 2.038 Å in other chloro ruthenium Tp complexes.^{12,13} The $\text{Ru}(1)-\text{C}(4)$ bond length of 2.087(4) Å is typical for a $\text{Ru}-\text{C}$ single bond. The $\text{C}(4)-\text{C}(5)$ bond length of 1.332(5) Å is typical for a $\text{C}=\text{C}$ double bond, indicating the coordination of the sp^2 carbon of the vinyl group. However, the bond angle $\text{Ru}(1)-\text{C}(4)-\text{N}(1)$ of $93.0(2)^\circ$ is much smaller than that of an idealized C (sp^2) hybridization.

Reaction of 3 with CO in the Presence of MeOH. Reaction of **3** with CO in the presence of MeOH causes substitution of a phosphine ligand by CO followed by protonation of the three-membered ring by MeOH, possibly giving a vinylidene intermediate. This is then followed by addition of the MeO^- to yield the vinyl ether complex $\text{Tp}(\text{PPh}_3)(\text{CO})\text{RuC}(\text{OMe})=\text{C}(\text{Ph})\text{CH}_2\text{CN}$ (**9**). In the ^1H NMR spectrum of **9**, the two doublet resonances at δ 3.84 and 3.02 with $J_{\text{H-H}} = 16.8$ Hz are assigned to the gem-protons. In the ^{13}C NMR spectrum, two doublet resonances attributed to the CO group and vinyl $\text{C}\alpha$ appear at δ 204.2 (with $J_{\text{P-C}} = 15.1$ Hz) and 188.3 (with $J_{\text{P-C}} = 14.0$ Hz), respectively. The ν_{CO} stretching in the IR spectrum of **9** appears at 1957 cm^{-1} . In the absence of MeOH, the reaction gives an unstable complex, possibly a simple substitution product, $\text{Tp}(\text{PPh}_3)(\text{CO})\text{RuC}=\text{C}(\text{Ph})\text{CHCN}$ (**B**). We believe that the reaction may proceed through substitution as the first step, followed by opening of the cyclopropenyl ring by MeOH to give a

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Table 1. Crystal and Intensity Collection Data for $\text{Tp}(\text{PPh}_3)\text{Ru}(\text{C}_3\text{H}_3\text{NN})\text{C}=\text{C}(\text{Ph})\text{CH}_2\text{CN}$ (8a**) and $\text{Tp}(\text{PPh}_3)(\text{CO})\text{RuC}(\text{O})\text{CHPhCH}_2\text{CN}$ (**11**)**

mol formula	$\text{C}_{40}\text{H}_{34}\text{BN}_9\text{PRu}$ (8a)	$\text{C}_{38}\text{H}_{32}\text{BN}_7\text{O}_2\text{PRu}$ (11)
mol wt	783.61	761.56
space group	$P1$	$P1$
a , Å	11.6820(2)	10.9969(1)
b , Å	17.1746(2)	12.3088(1)
c , Å	19.7647(3)	13.3739(2)
α , deg	73.720(1)	84.618(1)
β , deg	81.073(1)	88.934(1)
γ , deg	89.822(1)	75.641(1)
V , Å ³	3756.94(10)	1745.97(3)
Z	4	2
cryst dims, mm ³	$0.25 \times 0.25 \times 0.20$	$0.40 \times 0.25 \times 0.10$
Mo K α radiation: γ , Å	0.71073	0.71073
θ range, deg	1.09–25.02	1.53–26.37
limiting indices	$-8 \leq h \leq 13$ $-20 \leq k \leq 19$ $-22 \leq l \leq 23$	$-13 \leq h \leq 11$ $-15 \leq k \leq 15$ $-16 \leq l \leq 16$
no. of rflns collected	21 248	14 140
no. of ind rflns	13 076	7080
max. and min. transmission	0.8944 and 0.7076	0.8273 and 0.7059
refinement method		full-matrix least-squares on F^2
no. of data/restraints/params	13076/0/938	7080/0/451
GOF	1.00	1.023
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0426$, $WR_2 = 0.0917$	$R1 = 0.0420$, $WR_2 = 0.0956$
R indices (all data)	$R1 = 0.0737$, $WR_2 = 0.1094$	$R1 = 0.0590$, $WR_2 = 0.1043$
$\Delta\rho$ (in final map), e/Å	−0.468, +0.593	−0.426, +0.917

Figure 1. ORTEP drawing of **8a** with thermal ellipsoids shown at the 50% probability level.

vinylidene ligand. Nucleophilic attack of MeO^- at the α -carbon atom of the vinylidene ligand would then give the final product (Scheme 3). In our previous paper, we reported that MeOH is able to open certain three-membered rings.⁵ The reaction of **9** with CF_3COOH in CH_2Cl_2 at room temperature ultimately leads to the formation of acylruthenium complex $\text{Tp}(\text{PPh}_3)(\text{CO})\text{Ru}-\text{C}(\text{O})\text{CH}(\text{Ph})\text{CH}_2\text{CN}$ (**11**). When the reaction is followed by ^1H NMR spectroscopy, initial formation of the cationic alkoxy carbene complex $[\text{Tp}(\text{PPh}_3)(\text{CO})\text{Ru}=\text{C}(\text{OMe})-\text{CH}(\text{Ph})\text{CH}_2\text{CN}][\text{CF}_3\text{COO}]$ (**10**) was apparent, then followed by a slow reaction to give complex **11**. Chisholm and co-workers¹⁴ reported a similar reaction of Pt complexes.

When **9** was treated with HOAc in CH_2Cl_2 , no reaction was observed. The ν_{CO} stretching bands of **10** and **11** appear at 1998 and 1983 cm^{-1} , respectively, in their IR spectra. The doublet resonance at δ 213.6 with $^2J_{\text{P-C}} = 13.4$ Hz in the ^{13}C NMR spectrum of **10** is

Table 2. Selected Bond Distances (Å) and Angles (deg) of $\text{Tp}(\text{PPh}_3)\text{Ru}(\text{C}_3\text{H}_3\text{NN})\text{C}=\text{C}(\text{Ph})\text{CH}_2\text{CN}$ (8a**)**

$\text{Ru}(1)-\text{N}(2)$	2.071(3)	$\text{Ru}(1)-\text{C}(4)$	2.087(4)
$\text{Ru}(1)-\text{N}(6)$	2.098(3)	$\text{Ru}(1)-\text{N}(4)$	2.142(3)
$\text{Ru}(1)-\text{N}(8)$	2.156(3)	$\text{Ru}(1)-\text{P}(1)$	2.2801(11)
$\text{N}(1)-\text{C}(1)$	1.361(5)	$\text{N}(2)-\text{C}(3)$	1.309(5)
$\text{N}(1)-\text{C}(4)$	1.461(5)	$\text{C}(1)-\text{C}(2)$	1.372(6)
$\text{N}(3)-\text{C}(7)$	1.125(6)	$\text{C}(2)-\text{C}(3)$	1.394(6)
$\text{C}(4)-\text{C}(5)$	1.332(5)	$\text{C}(5)-\text{C}(6)$	1.511(6)
$\text{C}(6)-\text{C}(7)$	1.486(7)	$\text{C}(5)-\text{C}(8)$	1.493(6)
$\text{N}(2)-\text{Ru}(1)-\text{C}(4)$	65.32(14)	$\text{N}(2)-\text{Ru}(1)-\text{C}(6)$	169.28(13)
$\text{C}(4)-\text{Ru}(1)-\text{N}(6)$	105.91(14)	$\text{N}(2)-\text{Ru}(1)-\text{N}(4)$	87.65(12)
$\text{C}(4)-\text{Ru}(1)-\text{N}(4)$	86.88(14)	$\text{N}(6)-\text{Ru}(1)-\text{N}(4)$	65.65(12)
$\text{N}(2)-\text{Ru}(1)-\text{N}(8)$	99.62(13)	$\text{C}(4)-\text{Ru}(1)-\text{N}(8)$	162.52(14)
$\text{N}(6)-\text{Ru}(1)-\text{N}(8)$	87.94(12)	$\text{N}(4)-\text{Ru}(1)-\text{N}(8)$	83.52(12)
$\text{N}(2)-\text{Ru}(1)-\text{P}(1)$	94.09(9)	$\text{C}(4)-\text{Ru}(1)-\text{P}(1)$	95.33(11)
$\text{N}(6)-\text{Ru}(1)-\text{P}(1)$	92.87(9)	$\text{N}(4)-\text{Ru}(1)-\text{P}(1)$	177.61(9)
$\text{N}(8)-\text{Ru}(1)-\text{P}(1)$	94.56(9)	$\text{N}(2)-\text{N}(1)-\text{C}(4)$	105.0(3)
$\text{N}(1)-\text{N}(2)-\text{Ru}(1)$	96.7(2)	$\text{N}(1)-\text{C}(4)-\text{Ru}(1)$	93.0(2)
$\text{C}(4)-\text{C}(5)-\text{C}(8)$	126.3(4)	$\text{C}(8)-\text{C}(5)-\text{C}(6)$	114.1(4)
$\text{N}(3)-\text{C}(7)-\text{C}(6)$	176.7(6)	$\text{C}(7)-\text{C}(6)-\text{C}(5)$	113.5(4)

assigned to the acyl carbon atom. The two characteristic ^{13}C doublet resonances at δ 319.9 (with $J_{\text{P-C}} = 10.0$ Hz) and 201.5 ($J_{\text{P-C}} = 12.8$ Hz) are assigned to the carbene $\text{C}\alpha$ and the terminal CO group, respectively. In the ^1H NMR spectrum of **11**, the two multiplet resonances at δ 3.75 and 3.21 are assigned to the CH_2CN group. Orange-red crystals of **11** were obtained by slow diffusion of hexane into the ether solution of **11** at 0 °C for 3 days. The structure of **11** is determined by X-ray diffraction analysis. An ORTEP diagram is shown in Figure 2, and Table 3 lists selected bond distances and angles. The geometry around the metal center of **11** is approximately octahedral. The $\text{C}(2)-\text{O}(2)$ bond length of 1.214(4) Å and the $\text{Ru}-\text{C}(2)-\text{C}(3)$ bond angle of 124.7(2)° are characteristic for an acyl group. The $\text{Ru}-\text{C}(2)$ bond length of 2.042(4) Å is typical of a $\text{Ru}-\text{C}$ single bond. The $\text{C}(1)-\text{O}(1)$ bond distance of 1.140(4) Å indicates terminal CO coordinate at the ruthenium center.

Concluding Remarks. The cyclopropenyl ruthenium complex **3** containing a Tp ligand was prepared from deprotonation of the vinylidene precursor. Unlike

Scheme 3

Figure 2. ORTEP drawing of **11** with thermal ellipsoids shown at the 50% probability level.**Table 3.** Selected Bond Distances (Å) and Angles (deg) of $\text{Tp}(\text{PPh}_3)(\text{CO})\text{RuC}(\text{O})\text{CH}(\text{Ph})\text{CH}_2\text{CN}$ (**11**)

Ru—C(1)	1.846(4)	Ru—C(2)	2.042(3)
Ru—N(1)	2.125(3)	Ru—N(5)	2.162(3)
Ru—N(3)	2.208(3)	Ru(1)—P(1)	2.3599(9)
C(1)—O(1)	1.140(5)	N(7)—C(5)	1.130(4)
C(2)—C(3)	1.571(5)	C(3)—C(4)	1.543(5)
C(4)—C(5)	1.456(5)	C(2)—O(2)	1.214(4)
C(1)—Ru—C(2)	94.42(13)	C(1)—Ru—N(1)	89.36(13)
C(2)—Ru—N(6)	90.38(11)	C(1)—Ru—N(5)	171.93(13)
C(2)—Ru—N(5)	88.83(12)	N(1)—Ru—N(5)	83.22(11)
C(1)—Ru—N(3)	89.20(12)	C(2)—Ru—N(3)	172.25(12)
N(1)—Ru—N(3)	82.80(10)	N(5)—Ru—N(3)	86.72(10)
C(1)—Ru—P(1)	92.69(11)	C(2)—Ru—P(1)	95.22(9)
N(1)—Ru—P(1)	173.87(8)	N(5)—Ru—P(1)	94.37(8)
O(1)—Ru—P(1)	91.45(7)	O(2)—C(2)—C(3)	114.1(3)
O(1)—C(1)—Ru	172.9(3)	O(2)—C(2)—Ru	121.1(2)
C(3)—C(2)—Ru	121.1(2)	C(4)—C(3)—C(2)	107.8(3)
N(7)—C(5)—C(4)	176.6(5)		

its Cp analogue, the Tp cyclopropenyl complex **3** undergoes facile phosphine substitution reaction with several donor molecules. This property was employed to prepare novel complexes of Ru. For example, CH_3 -

CN readily displaces one of the phosphine ligands of **3** to give a mixture of diastereomers in a 4:1 ratio. Reaction of **3** with pyrazole gives the metallacyclic product **8a** resulting from a displacement reaction followed by nucleophilic addition of the nitrogen atom to the C α . Reaction of **3** with CO in the presence of MeOH follows a similar pathway to yield the vinyl ether complex **9**.

Experimental Section

General Procedure. 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, while THF was from Na/ketyl. All other solvents and reagents were of reagent grade and 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 δ units with residual protons in the solvent as an internal standard (CDCl_3 , δ 7.24; CD_3CN , δ 1.93; $\text{C}_2\text{D}_6\text{CO}$, δ 2.04). FAB mass spectra were recorded on a JEOL SX-102A spectrometer. $\text{Tp}(\text{PPh}_3)_2\text{RuCl}^+$ was prepared by following the method reported in the literature. Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instruments at National Taiwan University.

Preparation of $\text{Tp}(\text{PPh}_3)_2\text{Ru}-\text{C}\equiv\text{C}-\text{Ph}$ (1**).** To a 50 mL MeOH solution of $\text{Tp}(\text{PPh}_3)_2\text{RuCl}$ (3.93 g, 4.50 mmol) were added excess phenylacetylene (4.17 mL, 10 equiv) and excess Et_3N , and the solution was heated to reflux for 90 min. The yellow precipitates formed and, after cooling, were filtered off and washed with MeOH and hexane. This yellow solid product was dried under vacuum to give compound **1** (3.34 g, 79% yield). Spectroscopic data for **1**: ^1H NMR (CDCl_3): δ 7.58 (d, $J_{\text{H-H}} = 2.1$ Hz, 1H, Tp), 7.40 (d, $J_{\text{H-H}} = 2.1$ Hz, 2H, Tp), 7.24–6.91 (m, PPh_3 , Tp), 5.54 (t, $J_{\text{H-H}} = 2.1$ Hz, 2H, Tp), 5.31 (t, $J_{\text{H-H}} = 2.1$ Hz, 1H, Tp), 5.20 (d, $J_{\text{H-H}} = 2.1$ Hz, 1H, Tp). ^{13}C NMR (acetone): δ 135.8 (t, $J_{\text{P-C}} = 12.3$ Hz, C α), 145.7–122.7 (Ph, Tp, PPh_3 , C β). ^{31}P NMR (CDCl_3): δ 48.6. MS (FAB) m/z : 940.1 (M^+), 678.1 ($\text{M}^+ - \text{PPh}_3$), 577.1 ($\text{M}^+ - \text{PPh}_3$, C $_2\text{Ph}$), 363.0 ($\text{M}^+ - \text{PPh}_3$, C $_2\text{Ph}$, Tp). Anal. Calcd for $\text{C}_{53}\text{H}_{44}\text{N}_6\text{BP}_2\text{Ru}$ (938.75): C, 67.81; H, 4.72; N, 8.95. Found: C, 68.07; H, 4.54; N, 8.45.

Synthesis of the Vinylidene complex $[\text{Tp}(\text{PPh}_3)_2\text{Ru}=\text{C}=\text{C}(\text{Ph})\text{CH}_2\text{CN}]\text{I}$ (2**).** To a Schlenk flask charged with

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complex **1** (3.10 g, 3.30 mmol) in 50 mL of CH_2Cl_2 was added ICH_2CN (0.46 mL, 3.5 mmol). The clear solution was stirred for 16 h, and then the solvent was reduced to about 5 mL. This mixture was slowly added to 90 mL of a vigorously stirred diethyl ether solution. The green precipitate thus formed was filtered off and washed with diethyl ether and hexane to give compound **2** (3.29 g, 90%). Spectroscopic data for **2**: ^1H NMR (CDCl_3): δ 7.89 (br, 1H, Tp), 7.62 (br, 2H, Tp), 7.42–6.94 (m, PPh_3 , C_2Ph , Ph), 6.78 (br, 1H, Tp), 6.66 (br, 1H, Tp), 5.73 (br, 2H, Tp), 5.60 (br, 1H, Tp), 5.47 (br, 1H, Tp), 3.08 (s, 2H, CH_2). ^{13}C NMR (CDCl_3): δ 375.3 (t, $J_{\text{P-C}} = 16.5$ Hz, C α), 146.2–106.8 (m, Ph, Tp, PPh_3 , C β), 117.4 (CN), 11.4 (CH_2). ^{31}P NMR (CDCl_3): δ 36.5. MS (FAB) m/z : 980.5 ($\text{M}^+ - \text{I}$), 718.4 ($\text{M}^+ - \text{I}$, PPh_3), 577.2 ($\text{M}^+ - \text{I}$, PPh_3 , $\text{C}_2\text{PhCH}_2\text{CN}$). Anal. Calcd for $\text{C}_{55}\text{H}_{46}\text{N}_7\text{BIP}_2\text{Ru}$ (1105.7): C, 59.74; H, 4.19; N, 8.87. Found: C, 59.67; H, 4.25; N, 8.74.

Synthesis of the Cyclopropenyl Complex $\text{Tp}(\text{PPh}_3)_2\text{Ru}-\text{C}=\text{C}(\text{Ph})\text{CHCN}$ (3**).** To a solution of **2** (1.02 g, 0.92 mmol) in 20 mL of CH_2Cl_2 at 0 °C was added a solution of MeONa (10 mL, 1 M in MeOH). The mixture was stirred for 10 min, and the color changed from green to yellow. The solvent was removed under vacuum at 0 °C, and the solid residue was extracted with cool ether. The extract was filtered through Celite. Solvent of the filtrate was removed under vacuum to give **3** (0.82 g, 91% yield). Spectroscopic data for **3**: ^1H NMR (0 °C, acetone): δ 7.81 (d, $J_{\text{H-H}} = 2.1$ Hz, 1H, Tp), 7.77 (d, $J_{\text{H-H}} = 2.3$ Hz, 1H, Tp), 7.59 (d, $J_{\text{H-H}} = 2.3$ Hz, 1H, Tp), 7.40–6.94 (m, 33H, Ph, PPh_3), 6.89 (d, $J_{\text{H-H}} = 2.1$ Hz, 1H, Tp), 6.58–6.54 (m, 2H, Ph PPh_3), 5.97 (d, $J_{\text{H-H}} = 2.3$ Hz, 1H, Tp), 5.83 (d, $J_{\text{H-H}} = 2.3$ Hz, 1H, Tp), 5.62 (t, $J_{\text{H-H}} = 2.1$ Hz, 1H, Tp), 5.44 (t, $J_{\text{H-H}} = 2.3$ Hz, 1H, Tp), 5.39 (t, $J_{\text{H-H}} = 2.3$ Hz, 1H, Tp), 1.18 (s, 1H, C_2PhCHCN). ^{31}P NMR (0 °C, acetone): δ 48.8, 48.1 (AB, $J_{\text{P-P}} = 29.9$ Hz). MS (FAB) m/z : 980.4 ($\text{M}^+ + 1$), 718.3 ($\text{M}^+ + 1 - \text{PPh}_3$), 577.2 ($\text{M}^+ + 1 - \text{PPh}_3$, C_2PhCHCN).

Synthesis of the Cyclopropenyl Complex $\text{Tp}(\text{PPh}_3)-(\text{CH}_3\text{CN})\text{Ru}-\text{C}=\text{C}(\text{Ph})\text{CHCN}$ (4**).** To a solution of **3** (1.00 g, 1.02 mmol) in 20 mL of CH_2Cl_2 was added 10 mL of CH_3CN . The solution was stirred for 30 min, the color changed from yellow to brown, and then the solution was filtered through Celite. Solvent of the filtrate was removed under vacuum, and the residue was washed with hexane to give **4** (0.62 g, 80.0% yield). Two diastereomers of **4** in a 4:1 ratio are observed. The minor isomer in solution decomposed after 2 h at room temperature. Spectroscopic data for **4**: ^1H NMR (acetone) major compound: δ 7.85 (d, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 7.81 (d, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 7.69 (d, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 7.40–7.07 (m, Ph), 6.86 (1H, Tp), 6.78 (1H, Tp), 6.76 (1H, Tp), 6.02 (t, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 5.98 (t, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 5.85 (t, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 2.22 (s, 1H, CH_3CN), 1.08 (s, 1H, C_2PhCHCN); minor compound: δ 8.10 (1H, Tp), 7.40–7.07 (m, Ph, Tp, PPh_3), 5.74 (1H, Tp), 5.61 (1H, Tp), 5.96 (1H, Tp), 2.29 (s, 1H, CH_3CN), 1.20 (s, 1H, C_2PhCHCN). ^{13}C NMR (CDCl_3) major compound: δ 137.9 (d, $J_{\text{P-C}} = 11.4$ Hz, C α), 146.9–105.6 (m, Ph, PPh_3 , Tp), 123.7 (CH_3CN), 114.4 (CN), 3.6 (CH_3CN), 2.9 (CH). ^{31}P NMR (acetone): δ 56.7, 56.0 (4:1). MS (FAB) m/z : 759.3 ($\text{M}^+ + 1$), 718.3 ($\text{M}^+ + 1 - \text{CH}_3\text{CN}$), 577.1 ($\text{M}^+ + 1 - \text{CH}_3\text{CN}$, C_2PhCHCN). Anal. Calcd for $\text{C}_{39}\text{H}_{33}\text{N}_8\text{-BPRu}$ (756.56): C, 61.91; H, 4.40; N, 14.81. Found: C, 62.01; H, 4.46; N, 14.50.

Preparation of $[\text{Tp}(\text{PPh}_3)_2\text{Ru}=\text{C}=\text{C}(\text{Ph})\text{CH}(\text{CPh}_3)\text{CN}]\text{-PF}_6$ (5**).** To a solid mixture of **3** (0.25 g, 0.26 mmol) and $\text{Ph}_3\text{-CPF}_6$ (0.12 g, 0.3 mmol, in drybox) at 0 °C, was added 30 mL of CH_2Cl_2 . The mixture was stirred for 20 min, and the color changed from yellow to green. Then the solvent was removed under vacuum. The residual solid was washed with 2×20 mL of benzene and was dried under vacuum to give complex **5** (0.25 g, 69% yield). Spectroscopic data for **5**: ^1H NMR (acetone): δ 7.92 (d, $J_{\text{H-H}} = 2.3$ Hz, 1H, Tp), 7.83 (d, $J_{\text{H-H}} = 2.3$ Hz, 1H, Tp), 7.71 (d, $J_{\text{H-H}} = 2.3$ Hz, 1H, Tp), 7.4–6.9 (m, Tp, Ph), 6.83 (d, $J_{\text{H-H}} = 2.3$ Hz, 1H, Tp), 5.81 (d, $J_{\text{H-H}} = 2.2$

Hz, 1H, Tp), 5.66 (d, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 5.63 (t, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 5.54 (t, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 4.91 (s, 1H, CH). ^{13}C NMR (acetone): δ 371.3 (t, $J_{\text{P-C}} = 16.2$ Hz, C α), 146.1–106.3 (m, Ph, Tp, CPh_3 , PPh_3 , C β), 122.3 (CN), 21.2 (CH). ^{31}P NMR (acetone): δ 35.1, 33.6 (AB, $J_{\text{P-P}} = 26.7$ Hz). MS (FAB) m/z : 1222.1 ($\text{M}^+ - \text{PF}_6$), 978.8 ($\text{M}^+ - \text{PF}_6$, CPh_3), 838.8 ($\text{M}^+ - \text{PF}_6$, CPh_3 , C_2PhCHCN), 577.2 ($\text{M}^+ - \text{PF}_6$, CPh_3 , C_2PhCHCN , PPh_3). Anal. Calcd for $\text{C}_{74}\text{H}_{60}\text{N}_7\text{BP}_3\text{F}_6\text{Ru}$ (1366.06): C, 65.06; H, 4.43; N, 7.18. Found: C, 65.34; H, 4.41; N, 7.29.

Synthesis of $[\text{Tp}(\text{PPh}_3)_2\text{Ru}=\text{C}=\text{C}(\text{Ph})\text{CH}(\text{HgCl})\text{CN}]\text{Cl}$ (6**).** To a solid mixture of **3** (0.51 g, 0.52 mmol) and HgCl_2 (0.15 g, 0.52 mmol) at 0 °C was added 30 mL of CH_2Cl_2 . The mixture was stirred for 30 min, and the color changed from yellow to green. Then the solvent was removed under vacuum. The residual solid was extracted with 2×20 mL of ether, and the solvent was removed under vacuum to give complex **6** (0.45 g, 69% yield). Spectroscopic data for **6**: ^1H NMR (acetone): δ 8.01 (d, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 7.86 (d, $J_{\text{H-H}} = 2.3$ Hz, 1H, Tp), 7.75 (d, $J_{\text{H-H}} = 2.3$ Hz, 1H, Tp), 7.49–7.07 (m, Tp, Ph), 6.85 (d, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 5.85 (d, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 5.70 (d, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 5.68 (t, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 5.56 (t, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 3.19 (s, 1H, $\text{C}_2\text{-PhCHCNHg}$). ^{13}C NMR (CDCl_3): δ 375.1 (t, $J_{\text{P-C}} = 15.4$ Hz, C α), 146.8–107.5 (m, Ph, Tp, PPh_3 , C β), 120.3 (CN), 23.1 (CH). ^{31}P NMR (acetone): δ 35.5, 34.1 (AB, $J_{\text{P-P}} = 26.9$ Hz). MS (FAB) m/z : 1214.3 ($\text{M}^+ + 1 - \text{Cl}$), 978.8 ($\text{M}^+ - \text{Cl}$, HgCl), 838.8 ($\text{M}^+ - \text{Cl}$, HgCl , C_2PhCHCN), 577 ($\text{M}^+ - \text{Cl}$, HgCl , $\text{C}_2\text{-PhCHCN}$, PPh_3). Anal. Calcd for $\text{C}_{55}\text{H}_{45}\text{N}_7\text{BCl}_2\text{HgP}_2\text{Ru}$ (1249.28): C, 52.87; H, 3.63; N, 7.85. Found: C, 52.42; H, 4.04; N, 8.07.

Synthesis of $[\text{Tp}(\text{PPh}_3)(\text{CH}_3\text{CN})\text{Ru}=\text{C}=\text{C}(\text{Ph})\text{CH}(\text{HgCl})\text{-CN}]\text{Cl}$ (7**).** To a solid mixture of **4** (0.17 g, 0.17 mmol) and HgCl_2 (0.046 g, 0.17 mmol) was added 30 mL of CH_2Cl_2 . The mixture was stirred for 10 min, and then the solvent was removed under vacuum. The residual solid was extracted with 2×20 mL of ether, and after filtration, the solvent was removed under vacuum to give **7** (0.12 g, 73% yield). Spectroscopic data for **7**: ^1H NMR (acetone): δ 7.78 (d, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 7.76 (d, $J_{\text{H-H}} = 2.3$ Hz, 1H, Tp), 7.75 (d, $J_{\text{H-H}} = 2.3$ Hz, 1H, Tp), 7.43–7.03 (m, Tp, Ph), 6.40 (d, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 6.33 (br, 1H, Tp), 6.10 (t, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 5.93 (t, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 3.69 (s, 1H, $\text{C}_2\text{PhCHCNHg}$), 2.45 (s, 3H, CH_3CN). ^{13}C NMR (acetone): δ 369.3 (d, $J_{\text{P-C}} = 16.1$ Hz, C α), 146.8–107.5 (m, Ph, Tp, PPh_3 , C β), 135.0 ($\text{CH}_3\text{-CN}$), 124.6 (CN), 25.1 (CH), 4.6 (CH_3CN). ^{31}P NMR (acetone): δ 45.9. MS (FAB) m/z : 994.8 ($\text{M}^+ - \text{Cl}$), 758.8 ($\text{M}^+ - \text{Cl}$, HgCl), 618.4 ($\text{M}^+ - \text{Cl}$, HgCl , C_2PhCHCN), 577.2 ($\text{M}^+ - \text{Cl}$, HgCl , C_2PhCHCN , CH_3CN).

Reaction of **6 with MeONa .** To a solution of **6** (0.43 g, 0.34 mmol) in 20 mL of CH_2Cl_2 at 0 °C was added a solution of MeONa (1 mL, 1 M in MeOH). The mixture was stirred for 10 min, and then the solvent was removed at 0 °C under vacuum, the solid residue was extracted with cool ether, and the extract was filtered through Celite. Solvent of the filtrate was removed under vacuum to give **3** (0.245 g, 71% yield).

Reaction of **7 with MeONa .** To a solution of **7** (0.37 g, 0.35 mmol) in 20 mL of CH_2Cl_2 at 0 °C was added a solution of MeONa (1 mL, 1 M in MeOH). The mixture was stirred for 25 min, and the color changed from green to yellow. The solvent was removed at 0 °C under vacuum, the solid residue was extracted with cool ether, and the extract was filtered through Celite. Solvent of the filtrate was removed under vacuum to give **4** (0.17 g, 63% yield).

Preparation of $\text{Tp}(\text{PPh}_3)\text{Ru}(\text{C}_3\text{H}_3\text{NN})\text{C}=\text{C}(\text{Ph})\text{CH}_2\text{CN}$ (8a**).** To a solid mixture of **3** (1.02 g, 1.02 mmol) and pyrazole (0.07 g, 1.02 mmol) was added 30 mL of CH_2Cl_2 . The mixture was stirred for 60 min, and the color changed from yellow to bright yellow. Then the solvent was removed under vacuum. The residual solid was extracted with 2×20 mL of ether, and the solvent was filtered through Celite. Solvent of the resulting

solution was removed under vacuum to give **8a** (0.61 g, 79% yield). Spectroscopic data for **8a**: ^1H NMR (acetone): δ 7.84 (d, $J_{\text{H-H}} = 2.1$ Hz, 1H, Tp), 7.83 (d, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 7.82 (d, $J_{\text{H-H}} = 2.1$ Hz, 1H, TP), 7.43–7.10 (m, Ph, Tp), 7.15 (d, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 7.08 (d, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 7.02 (d, $J_{\text{H-H}} = 2.1$ Hz, 1H, Tp), 6.68 (d, $J_{\text{H-H}} = 2.1$ Hz, 1H, Tp), 6.17 (t, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 5.97 (t, $J_{\text{H-H}} = 2.1$ Hz, 1H, Tp), 5.94 (d, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 5.85 (t, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 5.61 (t, $J_{\text{H-H}} = 2.1$ Hz, 1H, Tp), 3.35 (d, $J_{\text{H-H}} = 17.3$ Hz, 1H, $\text{C}_2\text{PhCHHCN}$), 3.18 (d, $J_{\text{H-H}} = 17.3$ Hz, 1H, $\text{C}_2\text{-PhCHHCN}$). ^{13}C NMR (acetone): δ 163.3 (d, $J_{\text{P-C}} = 12.3$ Hz), 147.4–127.1 (Ph, PPh_3 , Tp), 119.6 (CN), 14.1 ($\text{C}_2\text{PhCH}_2\text{CN}$). ^{31}P NMR (acetone): δ 61.3. MS (FAB) m/z : 758.2 ($\text{M}^+ + 1$), 718.1 ($\text{M}^+ - \text{P}_2$), 577.1 ($\text{M}^+ - \text{P}_2$, C_2PhCHCN). Anal. Calcd for $\text{C}_{40}\text{H}_{34}\text{N}_9\text{BPRu}$ (938.75): C, 61.31; H, 4.37; N, 16.09. Found: C, 61.47; H, 4.44; N, 16.30. An intermediate was observed if the reaction was monitored by NMR spectroscopy within 20 min. Spectroscopic data for **A**: ^1H NMR (acetone): δ 8.03 (br, 1H, Tp), 7.96 (br, 1H, Tp), 7.83 (br, 1H, Tp), 7.43–7.10 (m, Ph, Tp), 7.65 (br, 1H, Tp), 6.53 (br, 1H, Tp), 6.24 (br, 1H, Tp), 6.03 (br, 1H, Tp), 5.83 (br, 1H, Tp), 5.40 (br, 1H, Tp), 4.40, 4.11 (two d, $J_{\text{H-H}} = 18.4$ Hz, 2H, CH_2CN). ^{31}P NMR (acetone): δ 36.7.

Preparation of $\text{Tp}(\text{PPh}_3)\text{Ru}(\text{Me}_2\text{C}_3\text{HNN})\text{C}=\text{C}(\text{Ph})\text{CH}_2\text{-CN}$ (8b**).** To a solid mixture of **5b** (0.40 g, 0.41 mmol) and 3,5-dimethylpyrazole (0.056 g, 0.82 mmol) was added 30 mL of CH_2Cl_2 . The mixture was stirred for 20 min, and then the solvent was removed under vacuum. The residual solid was extracted with 2×20 mL of ether, and the solution was filtered through Celite. Solvent of the filtrate was removed under vacuum to give **8b** (0.163 g, 49% yield). Spectroscopic data for **8b**: ^1H NMR (acetone): δ 7.81 (d, $J_{\text{H-H}} = 2.0$ Hz, 1H, Tp), 7.51 (d, $J_{\text{H-H}} = 2.0$ Hz, 1H, Tp), 7.42 (d, $J_{\text{H-H}} = 2.0$ Hz, 1H, Tp), 7.43–6.84 (m, Ph, Tp), 6.60 (d, $J_{\text{H-H}} = 2.1$ Hz, 1H, Tp), 6.13 (t, $J_{\text{H-H}} = 2.0$ Hz, 1H, Tp), 5.97 (t, $J_{\text{H-H}} = 2.1$ Hz, 1H, Tp), 5.94 (d, $J_{\text{H-H}} = 2.1$ Hz, 1H, Tp), 5.61 (t, $J_{\text{H-H}} = 2.0$ Hz, 1H, Tp), 3.25, 3.17 (two d, $J_{\text{H-H}} = 17.1$ Hz, 2H, CH_2CN), 2.38, 2.13 (s, 3H, $(\text{CH}_3)_2\text{C}_3\text{HNN}$). ^{13}C NMR (acetone): δ 162.2 (d, $J_{\text{P-C}} = 12.6$ Hz), 146.1–127.1 (PPh_3 , Tp, Ph), 118.7 (CN), 15.3 ($\text{C}_2\text{PhCH}_2\text{CN}$), 16.8, 15.3 ($(\text{CH}_3)_2\text{C}_3\text{HNN}$). ^{31}P NMR (acetone): δ 61.0. MS (FAB) m/z : 814.2 (M^+), 718.1 ($\text{M}^+ - \text{Me}_2\text{C}_3\text{HNN}$), 577.1 ($\text{M}^+ - \text{Me}_2\text{C}_3\text{HNN}$, C_2PhCHCN).

Synthesis of $\text{Tp}(\text{PPh}_3)(\text{CO})\text{RuC}(\text{OMe})=\text{C}(\text{Ph})\text{CH}_2\text{CN}$ (9**).** A solution of **3** (1.5 g, 1.53 mmol) was dissolved in methanol under CO atmosphere. After stirring for 50 min, the yellow solution became brown. The solution was filtered through Celite, and the solvent of the resulting solution was removed under vacuum to give the product **9** (1.01 g, 85% yield). Spectroscopic data for **9**: IR (acetone): ν_{CO} 1957 cm^{-1} (s). ^1H NMR (acetone): δ 8.00 (d, $J_{\text{H-H}} = 1.9$ Hz, 1H, Tp), 7.82 (m, 2H, Tp), 7.78 (d, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 7.52–7.03 (m, Ph, Tp), 6.34 (d, $J_{\text{H-H}} = 1.9$ Hz, 1H, Tp), 6.27 (t, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 5.92 (t, $J_{\text{H-H}} = 2.2$ Hz, 1H, Tp), 5.82 (d, $J_{\text{H-H}} = 1.9$ Hz, 1H, Tp), 3.84 (d, $J_{\text{H-H}} = 16.8$ Hz, 1H, $\text{C}_2\text{PhCHHCN}$), 3.02 (d, $J_{\text{H-H}} = 16.8$ Hz, 1H, $\text{C}_2\text{PhCHHCN}$), 2.85 (s, 3H, OMe). ^{13}C NMR (acetone): δ 204.2 (d, $J_{\text{P-C}} = 15.1$ Hz, CO), 188.3 (d, $J_{\text{P-C}} = 14.0$ Hz, C α), 146.5–124.5 (Ph), 119.9 (CN), 56.1 (OMe), 22.4 ($\text{C}_2\text{PhCH}_2\text{CN}$). ^{31}P NMR (acetone): δ 46.9. MS (FAB) m/z : 777.3 (M^+), 605.2 ($\text{M}^+ - (\text{OMe})\text{C}=\text{C}(\text{Ph})(\text{CH}_2\text{CN})$), 577.1 ($\text{M}^+ - (\text{OMe})\text{C}=\text{C}(\text{Ph})(\text{CH}_2\text{CN})$, $-\text{CO}$). Anal. Calcd for $\text{C}_{39}\text{H}_{34}\text{O}_2\text{N}_7\text{BPRu}$ (775.56): C, 60.39; H, 4.42; N, 16.09. Found: C, 60.71; H, 4.51; N, 16.41.

Synthesis of $[\text{Tp}(\text{PPh}_3)(\text{CO})\text{Ru}=\text{C}(\text{OMe})\text{CH}(\text{Ph})\text{CH}_2\text{CN}][\text{CF}_3\text{COO}]$ (10**).** Complex **9** (0.072 g, 0.093 mmol) was dissolved in 0.5 mL of $\text{CD}_3\text{C}(\text{O})\text{CD}_3$ at 0°C , and CF_3COOH (0.03

mL) was added. After 5 min, the solvent was removed under vacuum, and the product was washed with hexane and was identified as **10**. Spectroscopic data for **10**: IR (acetone): ν_{CO} 1998 cm^{-1} (s). ^1H NMR (acetone): δ 8.38 (br, 1H, Tp), 8.10 (br, 1H, Tp), 7.98–7.05 (m, Ph, Tp), 6.67 (br, 1H, Tp), 6.35 (br, 1H, Tp), 6.30 (br, 1H, Tp), 6.10 (br, 1H, Tp), 5.51 (br, 1H, Tp), 5.31 (dd, $J_{\text{H-H}} = 5.4$ Hz, $J_{\text{H-H}} = 10.1$ Hz, 1H, $\text{CCHPhCH}_2\text{-CN}$), 4.78 (s, 3H, OMe), 3.31 (m, 2H, $\text{C}_2\text{PhCH}_2\text{CN}$). ^{13}C NMR (acetone): δ 319.9 (d, $J_{\text{P-C}} = 10.0$ Hz, C α), 201.5 (d, $J_{\text{P-C}} = 12.8$ Hz, CO), 162.2 (q, $J_{\text{F-C}} = 43.1$ Hz, CF_3COO), 146.5–123.5 (Ph), 118.7 (q, $J_{\text{F-C}} = 282.0$ Hz, CF_3COO), 117.5 (CN), 70.4 (OMe), 64.2 ($\text{CCHPhCH}_2\text{CN}$), 29.0 ($\text{C}_2\text{PhCH}_2\text{CN}$). ^{31}P NMR (acetone): δ 36.9. MS (FAB) m/z : 778.3 (M^+), 605.2 ($\text{M}^+ - (\text{OMe})\text{CH}(\text{Ph})(\text{CH}_2\text{CN})$), 577.1 ($\text{M}^+ - (\text{OMe})\text{CH}(\text{Ph})(\text{CH}_2\text{CN})$, $-\text{CO}$).

Synthesis of $\text{Tp}(\text{PPh}_3)(\text{CO})\text{RuC}(\text{O})\text{CH}(\text{Ph})\text{CH}_2\text{CN}$ (11**).** Complex **9** (0.072 g, 0.093 mmol) was dissolved in 0.5 mL of $\text{CD}_3\text{C}(\text{O})\text{CD}_3$ at 0°C , and CF_3COOH (0.03 mL) was added. After 36 h, the solvent was removed under vacuum, and the product was washed with hexane and was identified as **11**. Spectroscopic data for **11**: IR (acetone): ν_{CO} 1983 cm^{-1} (s). ^1H NMR (acetone): δ 7.98–7.11 (m, Ph, Tp), 6.49 (br, 1H, Tp), 6.24 (br, 1H, Tp), 6.04 (br, 1H, Tp), 5.99 (br, 1H, Tp), 3.75, 3.21 (m, 2H, CH_2CN), 3.21 (m, 1H, $\text{C}_2\text{PhCHHCN}$), 2.41 (m, 1H, $\text{C}_2\text{HPhCH}_2\text{CN}$). ^{13}C NMR (acetone): δ 213.6 (d, $J_{\text{P-C}} = 13.4$ Hz, C α), 207.5 (d, $J_{\text{P-C}} = 12.6$ Hz, CO), 146.5–123.5 (Ph), 119.7 (CN), 54.6 ($\text{CCHPhCH}_2\text{CN}$), 24.0 ($\text{C}_2\text{PhCH}_2\text{CN}$). ^{31}P NMR (acetone): δ 41.3. MS (FAB) m/z : 761.2 (M^+), 605.2 ($\text{M}^+ - \text{C}(\text{O})\text{CH}(\text{Ph})(\text{CH}_2\text{CN})$), 577.1 ($\text{M}^+ - \text{C}(\text{O})\text{CH}(\text{Ph})(\text{CH}_2\text{CN})$, $-\text{CO}$). Anal. Calcd for $\text{C}_{38}\text{H}_{31}\text{O}_2\text{N}_7\text{BPRu}$ (760.53): C, 60.01; H, 4.11; N, 12.89. Found: C, 59.87; H, 3.95; N, 13.18.

X-ray Analysis. Dark red crystals of **8a** suitable for X-ray diffraction study were grown directly from CH_2Cl_2 . A suitable single crystal of dimensions $0.25 \times 0.25 \times 0.20$ mm 3 was glued to a glass fiber and mounted on an SMART CCD diffractometer. The data were collected using 3 kW sealed-tube molybdenum K α radiation ($T = 295$ K). Exposure time was 5 s per frame. Sadabs (Siemens area detector absorption) absorption correction was applied, and decay was negligible. Data were processed and the structure was solved and refined by the SHELXTL program. The structure was solved using direct methods and confirmed by Patterson methods refining on intensities of all data (13 076 reflections) to give $R1 = 0.0426$ and $wR2 = 0.0917$ for 13076 unique observed reflections ($I > 2\sigma(I)$). Hydrogen atoms were placed geometrically using the riding model with thermal parameters set to 1.2 times that for the atom to which the hydrogen is attached and 1.5 times that for the methyl hydrogens.

The procedures for the structure determination of **11** were similar to that of **8a**. The final residuals of the refinement $R1$ ($wR2$) were 0.042 (0.0956). Final values of all refined atomic positional parameters (with esd's) and tables of thermal parameters are given in the Supporting Information.

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Supporting Information Available: Tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom positions for **8a** and **11**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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