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Reactions of Ruthenium Cyclopropenyl Complexes Containing Pentamethylcyclopentadienyl Ligands

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Deprotonation of cationic pentamethylcyclopentadienyl dppp ruthenium vinylidene complexes containing electron-withdrawing groups at the vinylidene ligand yielded cyclopropenyl complexes $[\text{Ru}]\text{-C}=\text{C}(\text{Ph})\text{CHR}$ ($[\text{Ru}] = (\eta^5\text{-C}_5\text{Me}_5)(\text{dppp})\text{Ru}$, $\text{dppp} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$, $\text{R} = \text{CN}$, **3a**; $\text{R} = \text{CO}_2\text{CH}_3$, **3b**). Insertion of acetone into the three-membered ring of **3a** gave the neutral dihydrofuranyl complex $[\text{Ru}]\text{-C}=\text{C}(\text{Ph})\text{CH}(\text{CN})\text{CMe}_2\text{O}$ (**4**). Electrophilic addition at C_β of **4** afforded cationic carbene complexes $[[\text{Ru}]=\text{CC}(\text{R}')(\text{Ph})\text{CH}(\text{CN})\text{C}(\text{CH}_3)_2\text{O}]^+$ ($\text{R}' = \text{CH}_2\text{CN}$, **5a**; $\text{R}' = \text{CH}_2\text{CO}_2\text{CH}_3$, **5b**; $\text{R}' = \text{H}$, **7**; $\text{R}' = \text{HgCl}$, **8**). Complexes **5a** and **5b** transformed to $[[\text{Ru}]=\text{CC}(\text{Ph})=\text{C}(\text{CN})\text{C}(\text{CH}_3)_2\text{O}]^+$ (**6**) by elimination of small organic molecules. Reactivity of ruthenium complexes with a C_5Me_5 ligand is different from those with a C_5H_5 ligand and could be ascribed to electronic and steric effects. Reaction of $[\text{Ru}]\text{N}_3$ with ICH_2CN gave $[\text{Ru}]\text{-NCH}_2\text{I}$ (**11**). Crystal structures of complexes **3a**, **4**, **6**, **7**, and **11** are also reported.

Introduction

Metal vinylidene complexes have attracted considerable attention since they offer the possibility of development of new types of organometallic intermediates that may have unusual reactivity.^{1–4} Extensive reviews on this subject have appeared recently.^{5–7} The best entry into the transition metal vinylidene complexes is the addition of electrophiles to the electron-rich carbon of metal alkynyl complexes.^{8–18} A theoretical study of

vinylidene complexes indicated localization of electron density on C_β (HOMO) and the electron deficiency at C_α .^{19,20} A study of the reaction of alcohols with ruthenium vinylidene complexes indicated that electron-withdrawing groups on the acetylide unit or on the metal facilitate nucleophilic attack on C_α .²¹

Recently we demonstrated that the presence of an electron-withdrawing group at C_γ of the vinylidene ligand combined with the cationic character of the ruthenium complex enhances the acidity of the proton at C_γ . Thus deprotonation of such complexes could be readily achieved, and subsequent intramolecular cycloaddition could lead to the formation of cyclopropenyl complexes.^{1,2,22,23} For example, $[\text{Cp}(\text{PPh}_3)_2\text{Ru}=\text{C}(\text{Ph})\text{-CH}_2\text{CN}]^+$ was found to undergo deprotonation to afford

the cyclopropenyl complex $\text{Cp}(\text{PPh}_3)_2\text{Ru}=\text{C}(\text{Ph})\text{CHCN}$. Unfortunately, without a methoxy substituent, the three-membered ring readily undergoes electrophilic addition to cause ring opening in the presence of acid or other electrophiles. The presence of a methoxy substituent in the cyclopropenyl ring enhances the stability of the three-membered ring, and protonation of such a ruthenium complex yields a cyclopropenylum complex by loss of methanol. In our study, we also noticed that replacement of the Cp ligand with a Tp ligand²³ makes one of the phosphines labile, and a facile substitution reaction was observed for Tp ruthenium cyclopropenyl complexes. To extend the breadth, we

[†] National Overseas Chinese Student University Preparation School.

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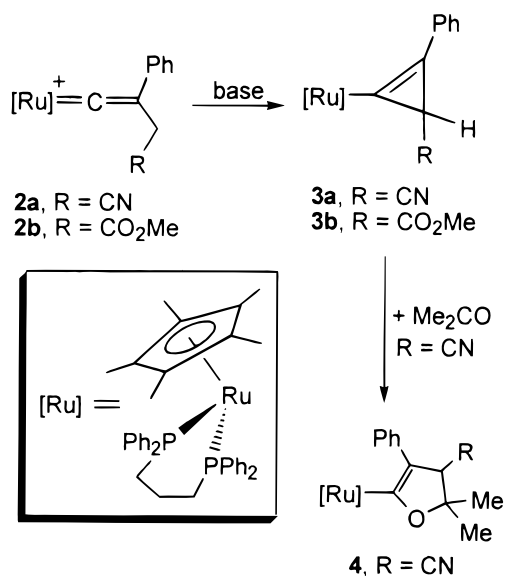
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Scheme 1



have explored the effect of C₅Me₅ (Cp*) on the chemistry of the ruthenium cyclopropenyl system. In this paper, we report an unprecedented acetone insertion into the cyclopropenyl ring, giving a dihydrofuranyl ligand and the electrophilic addition at C_β of the five-membered dihydrofuranyl ligand giving a carbene complex.

Results and Discussion

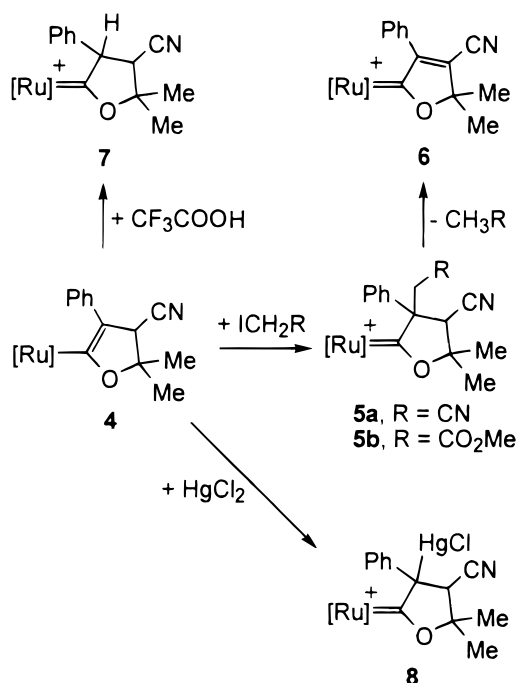
Synthesis of Ruthenium Vinylidene Complexes.

Treatment of [Ru]C≡Ph (**1**, [Ru] = Cp*(dppp)Ru, Cp* = η⁵-C₅Me₅, dppp = Ph₂PCH₂CH₂CH₂PPh₂) with ICH₂CN in CH₂Cl₂ afforded the cationic vinylidene complex [[Ru]=C=C(Ph)CH₂CN]⁺ (**2a**) in 85% yield (Scheme 1). Unlike other vinylidene complexes,⁵ which are generally prepared at room temperature, **2a** is prepared by heating a CH₂Cl₂ solution of **1** and ICH₂CN at reflux for 1 day. The steric effect of the Cp* ligand may hinder the electrophilic addition, therefore requiring mild heating and longer reaction times. Similarly, preparations of vinylidene complexes [[Ru]=C=C(Ph)CH₂R]⁺ (R = CO₂CH₃, **2b**; R = C₆F₅, **2c**; R = C₆H₅, **2d**; R = *p*-C₆H₄CN, **2e**; R = *p*-C₆H₄CF₃, **2f**) have produced high yields. All these reactions required mild heating and gave analytically pure complexes of various colors. The characteristic deshielded C_α resonances in the ¹³C NMR spectra of these vinylidene complexes appear as triplets in the region of δ = 343 ± 3. The ³¹P NMR resonance appears as a singlet at δ = 35 ± 1 in CDCl₃ at room temperature due to the fluxional behavior of the vinylidene ligand.^{24,25}

Cyclopropenation of Vinylidene Complexes.

Deprotonation of **2a** by *n*-Bu₄NOH is followed by the expected cyclization, yielding the cyclopropenyl complex [Ru]C≡C(Ph)CHCN (**3a**) (Scheme 1). Use of acetone or acetonitrile as a solvent gives a good yield, and use of other bases such as *n*-Bu₄NF (1 M in THF), DBU (1,8-diazabicyclo[5.4.0]undecene), or KOH (dissolved in a minimum amount of H₂O) also gives **3a** in comparable

Scheme 2



yield. The reaction gives yellow crystalline product in analytically pure form. Single crystals of **3a**, suitable for X-ray diffraction analysis, were obtained when the reaction is carried out at lower concentration. Complex **3a** is stable in air and soluble in CH₂Cl₂, CHCl₃, THF, and benzene, slightly soluble in acetone and diethyl ether, but insoluble in *n*-hexane, CH₃CN, and MeOH. The ³¹P NMR spectrum of **3a** displays two doublet resonances at δ 48.13 and 45.15 with ²J_{P-P} = 49.76 Hz in CDCl₃ arising from the presence of a stereogenic center in the three-membered ring. In the ¹H NMR spectrum of **3a**, the resonance of the methine proton appears at δ 1.07, and in the ¹³C{¹H} NMR spectrum, the triplet at δ 133.96 with ²J_{C-P} = 5.74 Hz is assigned to C_α.

The deprotonation/cyclopropenation reaction also occurs for **2b**, giving [Ru]C≡C(Ph)CHCO₂CH₃ (**3b**) in 77% yield. This reaction can only be carried out in acetone and only by using *n*-Bu₄NOH as a proton abstractor. Previously we reported that deprotonation of the analogous complex²² [(η⁵-C₅H₅)(PPh₃)₂Ru=C=C(Ph)CH₂CO₂CH₃]⁺ gave the cyclopropenyl complex as a kinetic product, which transformed to the furanyl complex in 1 h at room temperature. However, we did not observe such a transformation for **3b** in benzene after 3 days at room temperature. This could be due to steric repulsion between Cp* and the phenyl substituent on the cyclopropenyl ligand. The ³¹P NMR spectrum of **3b** also displays two doublet resonances at δ 47.73 and 43.00 with ²J_{P-P} = 50.18 Hz. In the ¹H NMR spectrum of **3b**, the resonance of the methine proton appears at δ 1.60.

Facile deprotonation of **2a** and **2b** indicates the acidic nature of the methylene protons, which may be ascribed to the combined effect of the cationic character and electron-withdrawing substituents of the vinylidene complexes. However, a similar reaction is not observed for complexes **2c–f** with *n*-Bu₄NF, DBU, or KOH. Analogous Cp vinylidene complexes undergo a deprotonation reaction to yield cyclization products.²² There-

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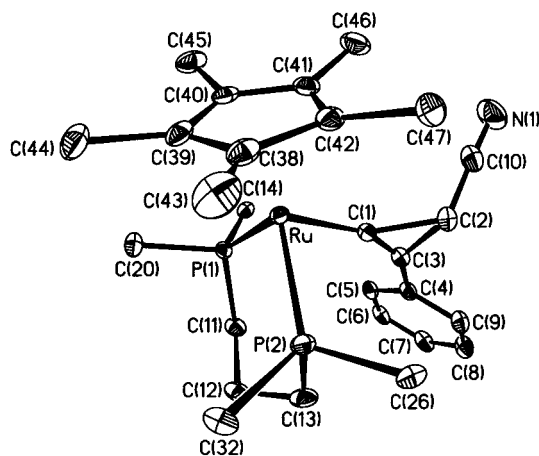


Figure 1. ORTEP drawing of **3a** with thermal ellipsoids shown at the 30% probability level. For phenyl groups on dppe, only the ipso carbons are shown.

fore, we conclude that, in the vinylidene system with a Cp^* ligand, a strong electron-withdrawing group on the vinylidene ligand is necessary to enhance acidity of the methylene protons for deprotonation.

Previous studies on metal cyclopropenyl derivatives^{26–30} include the synthesis of iron derivatives from the reaction of metal carbonylate anions with cyclopropenyl cations reported by Bartmann and Gompper,^{27,31} as well as CO insertion and ring-opening studies of such systems^{28,29} by Hughes and co-workers. We reported the synthesis and chemical reactivity of several neutral ruthenium cyclopropenyl complexes^{1,2,22–23} in which the metal bonds to one $\text{C}(\text{sp}^2)$ atom of the three-membered cyclopropenyl ring. A few structurally different cyclopropenylidene complexes, mostly prepared from dichlorocyclopropene,^{32,33} and a number of π -cyclopropene complexes^{34–37} are also known. The acidity of the aliphatic protons on the coordinated dppe ligand in a cationic iron vinylidene complex³⁸ has been employed for inducing the intramolecular cyclization between the dppe and the vinylidene ligand.

The molecular structure of **3a** has been confirmed by a single-crystal X-ray diffraction study. An ORTEP diagram is shown in Figure 1, and selected bond distances and angles are listed in Table 1. This complex adopts a distorted three-leg piano stool geometry. The Ru–C1 distance of 2.048(2) Å is typical for a Ru–C

Table 1. Selected Bond Distances (Å) and Angles (deg) of $(\eta^5\text{-C}_5\text{Me}_5)(\text{dppp})\text{RuC}=\text{C}(\text{Ph})\text{CHCN}$ (**3a**)

Ru–P1	2.2956(5)	Ru–P2	2.2934(5)
Ru–C1	2.048(2)	C1–C3	1.313(3)
C1–C2	1.601(3)	C2–C3	1.506(3)
C2–C10	1.448(3)	N1–C10	1.154(3)
C3–C4	1.469(3)		
P1–Ru–P2	92.45(2)	Ru–C1–C2	136.1(1)
Ru–C1–C3	160.4(3)	C1–C2–C3	49.9(1)
C1–Ru–P1	88.88(5)	C1–Ru–P2	81.88(5)
C2–C1–C3	61.3(1)	C2–C3–C1	68.8(1)
C1–C3–C4	155.5(2)	C2–C3–C4	135.4(2)
C3–C2–C10	118.2(2)	C1–C2–C10	121.8(2)

single bond, and the C1–C3 distance of 1.313(3) Å is a regular C=C double bond, indicating coordination of one sp^2 carbon of the cyclopropenyl ligand. Both bond angles Ru–C1–C3 and C1–C3–C4 (160.4(2)° and 155.5(2)°, respectively) are greater than that of an idealized sp^2 hybridization. The C1–C2 and C2–C3 bond lengths of 1.601(3) and 1.506(3) Å, respectively, are significantly different, conforming to the favorable cleavage of the C1–C2 bond.

Insertion of Acetone into the Cyclopropenyl Ring of **3a.** If the bright yellow solution of **3a** in acetone is stored at room temperature for 2 days, the color of the solution turns yellow-brown. The ^{31}P NMR spectrum of the mixture indicated formation of two new complexes

in a ratio of 2:1. The major product, $[\text{Ru}]\text{C}=\text{C}(\text{Ph})\text{CH}(\text{CN})\text{C}(\text{CH}_3)_2\text{O}$ (**4**), is formed by addition of an acetone molecule to the three-membered ring of **3a**, which is confirmed by single-crystal X-ray diffraction analysis. Complex **4** is air stable and soluble in THF, CH_2Cl_2 , CHCl_3 , and benzene, moderately soluble in acetone, acetonitrile, and methanol, and insoluble in hexane. Thermolysis of **4** at 60 °C afforded **1**. The organic portion from this reaction was not isolated. In the ^{31}P NMR spectrum of the mixture, two doublet resonances at δ 45.38 and 39.11 with $J_{\text{P-P}} = 52.12$ Hz are assigned to **4**. The ^1H NMR spectrum of **4** displays resonances at δ 1.09, 1.22, and 1.57 that are assignable to Cp^* , 2CH_3 , and CH, respectively.

Complex **4** was recrystallized from THF/hexane (1:3) to give single crystals, and its molecular structure was determined by a single-crystal X-ray diffraction study. An ORTEP diagram is shown in Figure 2, and selected bond distances and bond angles are given in Table 2. Complex **4** adopts a distorted three-leg piano stool geometry with the P1–Ru–P2, P1–Ru–C1, and P2–Ru–C1 angles being 90.78(8)°, 88.5(2)°, and 86.3(3)°, respectively. Insertion of an acetone molecule is clearly seen in the coordinated five-membered dihydrofuranyl ligand. The Ru–C1 distance of 2.101(7) Å is typical for a Ru–C single bond, and the C1–C3 distance of 1.371(10) Å indicates a C=C double bond. The O1–C1 and O1–C4 single bond lengths of 1.431(8) and 1.455(9) Å, respectively, are comparable. The Ru–C1–C2 bond angle of 136.7(5)° is slightly greater than an sp^2 hybridization bond angle; thus O1–C1–C2 and Ru–C1–O1 bond angles of 108.6(6)° and 113.8(4)°, respectively, are smaller.

Acetone is the only reagent found to undergo an insertion reaction to give **4**. Methyl isobutyl ketone, 2-butanone, and 3-pentanone have been used as sol-

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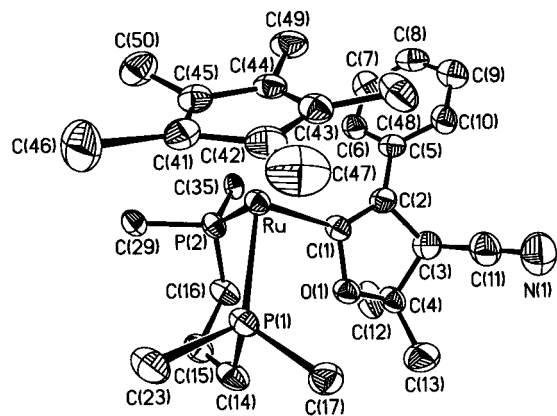


Figure 2. ORTEP drawing of **4** with thermal ellipsoids shown at the 30% probability level. For phenyl groups on dppp, only the ipso carbons are shown.

Table 2. Selected Bond Distances (Å) and Angles (deg) of

$(\eta^5\text{-C}_5\text{Me}_5)(\text{dppp})\text{RuC}=\text{C}(\text{Ph})\text{CH}(\text{CN})\text{C}(\text{CH}_3)_2\text{O}$ (**4**)

Ru–P1	2.321(2)	Ru–P2	2.283(2)
Ru–C1	2.101(7)	C1–C2	1.37(1)
C2–C3	1.55(1)	C3–C4	1.55(1)
C3–C11	1.50(2)	C11–N1	1.13(1)
C1–O1	1.431(8)	C4–O1	1.455(9)
C4–C12	1.46(1)	C4–C13	1.45(1)
Ru–C1–C2	136.7(5)	Ru–C1–O1	113.8(4)
C2–C1–O1	108.6(6)	C1–C2–C3	108.0(7)
C2–C3–C4	102.9(7)	C1–C2–C5	134.6(8)
C11–C3–C4	113.4(9)	C11–C3–C2	110.8(8)
C13–C4–O1	108.2(8)	O1–C4–C12	110.9(7)
O1–C3–C4	100.9(6)	C1–Ru–P1	88.5(2)
C1–Ru–P2	86.3(3)	P1–Ru–P2	90.78(8)
C3–C2–C5	117.2(7)	C3–C4–C12	110.0(9)
C3–C4–C13	118.0(8)	C12–C4–C13	108.6(9)

vents for the reaction of **2a** with *n*-Bu₄NOH. In these solvent systems, **3a** formed in good yield, but no insertion product was observed at room temperature. Addition of PhNCO, PhNCS, (CF₃)₂CO, or formaldehyde to a benzene solution of **3a** resulted in ring opening, yielding **2a**, and addition of propanal resulted in decomposition of **3a**, leading to **1**. The minor product of the reaction of **2a** with base in the presence of acetone was not isolated due to decomposition to **1** during chromatography. However, on the basis of the ³¹P NMR spectrum of the mixture displaying two doublet ³¹P resonances at δ 28.67, 11.77 (*J*_{P–P} = 52.21 Hz) assignable for this minor product and the mass spectrum of the mixture displaying only parent peaks of **4**, the inverted insertion mode giving [Ru]C=C(Ph)CH(CN)–OC(CH₃)₂ (**4'**) is speculated.

Electrophilic Additions of Ruthenium Cyclopentenyl Complex 4. Treatment of **4** with organic halides XCH₂R afforded cationic cyclic carbene complexes $[\text{Ru}]=\text{CC}(\text{CH}_2\text{R})(\text{Ph})\text{CH}(\text{CN})\text{C}(\text{CH}_3)_2\text{O}[\text{X}]$ (R = CN, X = I, **5a**; R = CO₂CH₃, X = Br, **5b**) in high yields. Both ³¹P NMR spectra display two doublet resonances: δ 37.30, 31.45 with *J*_{P–P} = 48.02 Hz and δ 37.38, 31.94 with *J*_{P–P} = 52.91 Hz, assignable to **5a** and **5b**, respectively. The five-membered ring contains two stereogenic carbon centers, and two diastereomers were expected. However, for each compound, we see only one set of two ³¹P doublets, indicating high diastereoselec-

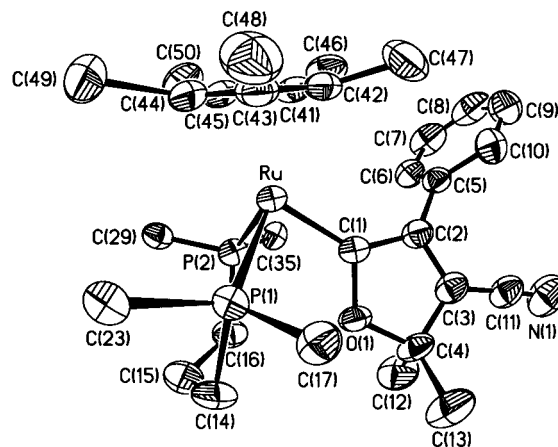


Figure 3. ORTEP drawing of **6** with thermal ellipsoids shown at the 30% probability level. For phenyl groups on dppp, only the ipso carbons are shown.

Table 3. Selected Bond Distances (Å) and Angles (deg) of

$(\eta^5\text{-C}_5\text{Me}_5)(\text{dppp})\text{Ru}=\text{CC}(\text{Ph})=\text{C}(\text{CN})\text{C}(\text{CH}_3)_2\text{O}$ (**6**)

Ru–P1	2.333(1)	Ru–P2	2.333(1)
Ru–C1	1.953(5)	C1–C2	1.500(7)
C2–C3	1.378(7)	O1–C1	1.375(6)
C3–C4	1.481(8)	O1–C4	1.462(6)
C3–C11	1.421(8)	C11–N1	1.136(7)
C4–C12	1.514(9)	C4–C13	1.517(7)
C1–Ru–P2	86.4(2)	P1–Ru–C1	86.9(1)
P1–Ru–P2	91.97(5)	O1–C1–C2	103.1(4)
Ru–C1–C2	137.1(4)	O1–C1–Ru	119.7(3)
C2–C3–C4	111.8(5)	C1–O1–C4	116.3(4)
C1–C2–C3	108.5(4)	C1–C2–C5	131.2(5)
C3–C2–C5	119.6(5)	C2–C3–C11	126.6(5)
C11–C3–C4	121.1(5)	O1–C4–C3	99.9(4)
C12–C4–C3	111.5(5)	O1–C4–C12	108.3(5)
C3–C4–C13	115.8(5)	O1–C4–C13	108.8(4)
C12–C4–C13	111.7(5)		

tivity. This is possibly due to the steric effect of the Cp* ligand. Spectroscopic data of **5** consist of a strongly deshielded C_α resonance as a triplet at around δ 290 in the ¹³C NMR spectrum.

Elimination of CH₃CN from **5a** in CDCl₃ generated the new cationic cyclic carbene complex $[\text{Ru}]=\text{CC}(\text{Ph})=\text{C}(\text{CN})\text{C}(\text{CH}_3)_2\text{O}[\text{I}]$ (**6**) (Scheme 2). The reaction was complete in 3 days at room temperature, and heating the solution accelerated the reaction. Complex **5b** also transformed to **6** in solution after 1 week at room temperature and in refluxing CHCl₃ after 1 day. Complex **6** can also be obtained directly by thermolysis of **4** in the presence of ICH₂CN or BrCH₂CO₂CH₃. The ³¹P NMR spectrum of **6** displays a singlet at δ 37.1, and, in the ¹³C NMR spectrum of **6**, the deshielded triplet C_α resonance at δ 275.0 is characteristic of a carbene complex.

The molecular structure of **6** has been confirmed by a single-crystal X-ray diffraction study. An ORTEP diagram is shown in Figure 3, and selected bond distances and bond angles are given in Table 3. This complex adopts a three-leg piano stool geometry with the P1–Ru–P2, P1–Ru–C1, and P2–Ru–C1 angles being 91.97(5)°, 86.93(14)°, and 86.4(2)°, respectively. The Ru–C1 distance of 1.953(5) Å is typical for a Ru=C double bond. In the five-membered ring, the C2–C3 bond distance of 1.378(7) Å indicates a double bond. The

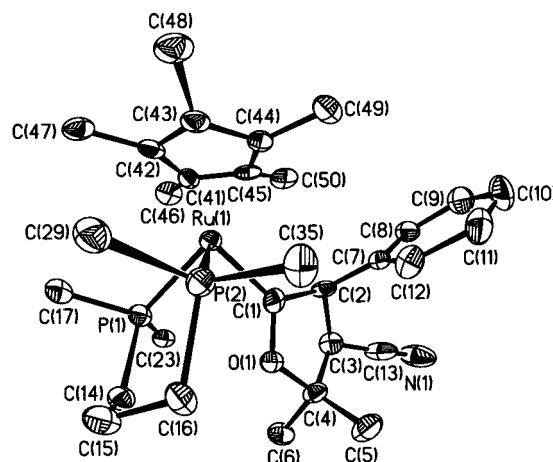
shorter O1–C1 bond lengths of 1.375(6) Å, relative to that of O1–C4 of 1.462(6) Å, indicates contribution of the lone pair of oxygen, thus leading to a stronger C(sp²)–O single bond. The C1–C2–C5 and C2–C3–C11 bond angles of 131.2(5)° and 126.6(5)°, respectively, are consistent with sp² hybridization for C2 and C3.

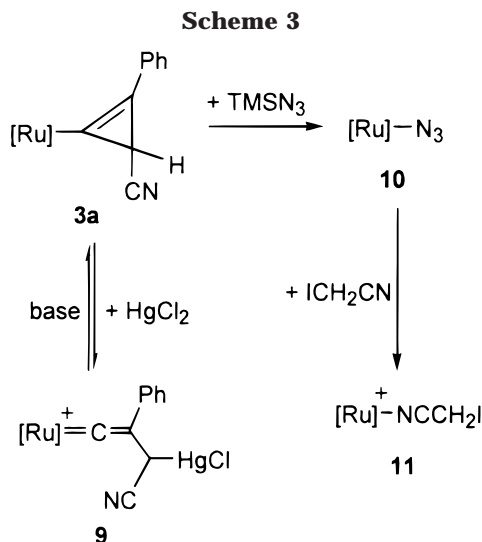
Protonation of **4** with CF₃COOH occurs also at C_β of the five-membered ring, yielding the carbene complex

$[[Ru]=CCH(Ph)CH(CN)C(CH_3)_2O][CF_3COO]$ (**7**) (Scheme 2). This reaction is faster compared to the reaction of **4** with XCH₂R (5 min vs 24 h at room temperature). The protonation resulted in formation of two diastereomers, giving two sets of doublets of doublets at δ 38.63, 32.97 (J_{P-P} = 48.03 Hz) and δ 37.09, 31.93 (J_{P-P} = 48.93 Hz) in a ratio of 20:1 in the ³¹P NMR spectrum. Purification by recrystallization gave only the major isomer. The characteristic C_α resonance of the major isomer of **7** appears as a triplet at δ 290.5 in the ¹³C NMR spectrum, and, in the ¹H NMR spectrum, two singlets appear at δ 5.13 and δ 1.59, assignable to the CHPh and CHCN groups of the five-membered ring, respectively. The FAB mass spectrum displays a parent peak at m/e 848.3 attributed to (M⁺ – CF₃COO). In solution, **7** slowly transformed to **6** by elimination of H₂. After 14 days at room temperature the transformation was not complete and the ratio of **7**:**6** was 4:1. Thermolysis of the solution caused decomposition of **7**.

Addition of HgCl₂ to **4** resulted in immediate formation of the blue carbene complex $[[Ru]=C(HgCl)(Ph)CH(CN)C(CH_3)_2O][Cl]$ (**8**). The presence of two stereogenic carbon centers in the cyclic ligand resulted in two sets of doublets of doublets at δ 37.8, 32.2 with J_{P-P} = 50.85 Hz and δ 37.75, 31.83 with J_{P-P} = 48.01 Hz in a ratio of 10:1 in the ³¹P NMR spectrum. The minor isomer escaped from purification by recrystallization again, since only the major one was obtained. The ¹³C NMR spectrum of the major isomer of **8** consists of strongly deshielded C_α resonance as a triplet at δ 309.7 in CDCl₃ at room temperature. No transformation of **8** to **6** is observed in CDCl₃ after 14 days. The lower diastereoselectivity of the mercuric chloride addition to **4** relative to that in protonation is somewhat surprising, and we do not have rationalization for this observation.

The molecular structure of **7** was confirmed by a single-crystal X-ray diffraction study. An ORTEP diagram is shown in Figure 4, and selected bond distances and bond angles are listed in Table 4. The Ru–C1 distance of 1.943(8) Å is typical for a Ru carbene system, and the C2–C3 bond length of 1.554(12) Å is a C–C single bond. The different O1–C1 and O1–C4 bond lengths of 1.33(1) and 1.49(1) Å, respectively, are consistent with other similar carbene complexes.³⁹ The Ru1–C1–C2 and O1–C1–Ru1 bond angles of 128.2(6)° and 125.2(6)°, respectively, are slightly greater than an sp² hybridization bond angle. The O1–C1–C2, C1–C2–C3, C2–C3–C4, and C3–C4–O1 bond angles of 106.2(7)°, 103.3(6)°, 105.0(7)°, and 100.7(6)°, respectively, are slightly smaller than a typical pentagonal





becoming a light orange after ca. 30 min, and, after 1 h, turning yellow again. The final product was recovered as $[\text{Ru}]\text{N}_3$ (**10**) (Scheme 3) in 78% yield. Recently⁴⁰ we reported reactions of Cp ruthenium cyclopropenyl complexes with TMSN_3 . The reaction of **3a** with TMSN_3 may proceed similarly, i.e., via electrophilic addition of a TMS group to the sp^3 carbon of the cyclopropenyl ring followed by hydrolysis. Nucleophilic addition of an N_3 anion at C_α and electrophilic addition of a second TMS unit at C_β followed by loss of N_2 then gives an N-coordinated nitrile complex. Substitution of the nitrile ligand by N_3^- occurs finally after 1 h to give **10**. The proton source of the reaction is believed to come from the small amount of water in solvent and in TMSN_3 (no attempt was made to dry TMSN_3 due to potential hazards) and protons incorporated into the product through hydrolysis of the TMS substituents. No attempt was made to isolate the organic product.

Interestingly, treatment of yellow complex **10** with excess ICH_2CN at room temperature afforded the brown N-coordinated iodoacetonitrile complex $\{[\text{Ru}]\text{NC}-\text{CH}_2\text{I}\}[\text{I}_3]$ (**11**) (Scheme 3). Surprisingly, no iodide addition was observed; instead the coordinated N_3^- is readily replaced by ICH_2CN without cleavage of the C–I bond. In the ^1H NMR spectrum of **11**, two singlet resonances at δ 4.50 and 1.54 are assigned to CH_2 and Cp^* , respectively. The ^{31}P NMR spectrum displays a singlet resonance at δ 35.01. In the ^{13}C NMR spectrum, resonances at δ 119.4, 50.9, and 9.7 are assigned to CN, CH_2 , and Cp^* , respectively. Complex **11** is stable in air and soluble in most polar solvents such as CH_2Cl_2 , acetone, acetonitrile, THF, and MeOH and moderately soluble in *n*-pentane and *n*-hexane.

The molecular structure of **11** was confirmed by a single-crystal X-ray diffraction study. An ORTEP diagram is shown in Figure 5, and selected bond distances and bond angles are given in Table 5. The metal center is coordinated to the nitrile nitrogen atom of ICH_2CN , and the counteranion is I_3^- . The Ru–N1 bond length of 2.027(5) Å is typical for a Ru–N dative bond. The N1–C2 bond length of 1.155(8) Å is typical for a C–N triple bond. The C2–C3 and C3–I1 bond lengths of 1.453(10) and 2.188(9) Å indicate a C–C single bond and C–I

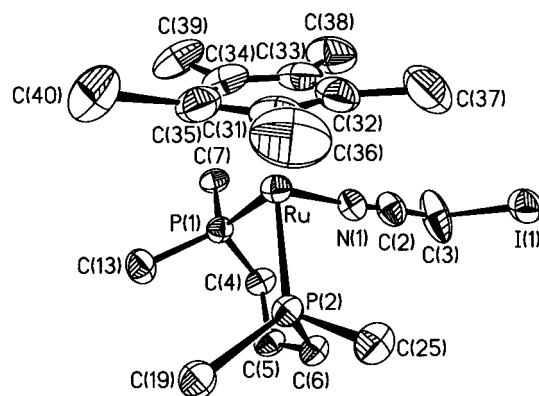


Figure 5. ORTEP drawing of **11** with thermal ellipsoids shown at the 30% probability level. For phenyl groups on dppp, only the ipso carbons are shown.

Table 5. Selected Bond Distances (Å) and Angles (deg) of $[(\eta^5\text{-C}_5\text{Me}_5)(\text{dppp})\text{RuNCCH}_2\text{I}][\text{I}_3]$ (**11**)

Ru–P1	2.334(2)	Ru–P2	2.334(1)
Ru–N1	2.027(5)	N1–C2	1.155(8)
C2–C3	1.45(1)	C3–I1	2.188(9)
P1–Ru–P2	86.09(5)	P1–Ru–N1	89.0(1)
P2–Ru–N1	87.2(1)	Ru–N1–C2	173.1(5)
N1–C2–C3	176.1(9)	C2–C3–I1	109.8(5)

single bond, respectively. The N1–C2–C3 angle of 176.1(9)° is close to linear, indicating a $\text{C}(\text{sp})$ hybridization. The C2–C3–I1 angle of 109.8(5)° is typical for that of an idealized $\text{C}(\text{sp}^3)$ hybridization.

Conclusions

Facile preparation of two neutral C_5Me_5 -dppp-Ru cyclopropenyl complexes was achieved by deprotonation of cationic vinylidene complexes with electron-withdrawing substituents such as $-\text{CN}$ and $-\text{CO}_2\text{CH}_3$ in acetone. Treatment of cationic vinylidene complexes containing relatively weaker electron-withdrawing substituents such as C_6F_5 , Ph, *p*- $\text{C}_6\text{H}_4\text{CN}$, and *p*- $\text{C}_6\text{H}_4\text{CF}_3$ with base failed to give similar result. Protonation of the ruthenium cyclopropenyl complexes regenerated the vinylidene complexes, showing the nucleophilic nature of the antecedent C_γ carbon of the cyclopropenyl ligand. Thus other electrophiles could also be added to this C_γ site by reactions with cyclopropenyl complexes. No conversion of **3b** to the ruthenium furanyl complex was observed regardless of much higher strain energy of the cyclopropenyl ring. An acetone insertion reaction was observed in the cyclopropenyl complex **3a**, yielding a neutral five-membered dihydrofuran complex **4** in moderate yield.

Electrophilic addition to **4** affords the cationic carbene complexes **5a** and **5b**. Complexes **5a** and **5b** are transformed to **6** by elimination of a small organic molecule. The significantly different reactivity of ruthenium complexes with a Cp^* ligand from those with a C_5H_5 ligand may be due to the electronic and steric effects. Treatment of **3** with $(\text{CH}_3)_3\text{SiN}_3$ afforded **10**, and subsequent reaction of **10** with ICH_2CN produced a novel N-coordinated nitrile complex **11**.

Experimental Section

General Procedures. All manipulations were performed under nitrogen using vacuum-line, drybox, and standard

Schlenk techniques. CH_2Cl_2 was distilled from CaH_2 , and diethyl ether and THF were distilled from sodium diphenylketyl. All other solvents and reagents were of reagent grade and were used 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 referenced to residual protons in the solvents (CDCl_3 , δ 7.24; acetone- d_6 , δ 2.04). FAB mass spectra were recorded on a JEOL SX-102A spectrometer. Complex $[\text{Ru}]\text{C}\equiv\text{CPh}$, **1**, was prepared following the methods reported in the literature.⁴¹ Elemental analyses and X-ray diffraction studies were carried out at the Regional Center of Analytical Instruments located at the National Taiwan University.

Synthesis of $[\text{Ru}]\text{C}\equiv\text{C}(\text{Ph})\text{CH}_2\text{CN}[\text{I}]$ (2a**).** A Schlenk flask was charged with ICH_2CN (240 μL , 3.3 mmol) and **1** (250 mg, 0.33 mmol) in 10 mL of CH_2Cl_2 . The mixture was heated to reflux for 24 h. After the solution was allowed to cool, the solvent was reduced to about 3 mL under vacuum and was added to 20 mL of a vigorously stirred diethyl ether solution. The pink powders thus formed were filtered and washed with 20 mL of *n*-hexane and 20 mL of diethyl ether and dried under vacuum to give the product **2a** (260 mg, 85% yield). Spectroscopic data for **2a** are as follows: ^1H NMR (CDCl_3) δ 7.47–6.82 (m, 25H, Ph), 3.22 (s, 2H, CH_2), 2.65 (m, 2PCH₂), 1.93 (m, PCH₂CH₂), 1.58 (s, 15H, 5CH₃); ^{31}P NMR (CDCl_3) δ 34.35; ^{13}C NMR (CDCl_3) δ 341.8 (t, C_α , $J_{\text{C-P}} = 17.9$ Hz), 133.3–127.8 (Ph), 119.4 (C_β), 118.6 (CN), 104.7 (Cp), 29.4 (t, PCH₂, $J_{\text{C-P}} = 17.9$ Hz), 21.3 (PCH₂CH₂), 17.4 (CH_2CN), 10.3 (5CH₃); MS (m/z , Ru^{102}) 790.2 ($\text{M}^+ - \text{I}$), 750.2 ($\text{M}^+ - \text{I} - \text{CH}_2\text{CN}$), 649.1 ($\text{M}^+ - \text{I} - \text{CH}_2\text{CN} - \text{CCPh}$). Anal. Calcd for $\text{C}_{47}\text{H}_{48}\text{NP}_2\text{RuI}$: C, 61.57; H, 5.28; N, 1.53. Found: C, 62.37; H, 5.45; N, 1.44.

Complexes $[\text{Ru}]\text{C}\equiv\text{C}(\text{Ph})\text{CH}_2\text{R}[\text{Br}]$ ($\text{R} = \text{CO}_2\text{CH}_3$, **2b** (85% yield); $\text{R} = \text{C}_6\text{F}_5$, **2c** (82% yield); $\text{R} = \text{Ph}$, **2d** (79% yield); $\text{R} = p\text{-C}_6\text{H}_4\text{CN}$, **2e** (83% yield); $\text{R} = p\text{-C}_6\text{H}_4\text{CF}_3$, **2f** (87% yield)) were prepared from the reaction of **1** with $\text{BrCH}_2\text{CO}_2\text{CH}_3$, $\text{BrCH}_2\text{C}_6\text{F}_5$, $\text{BrCH}_2\text{C}_6\text{H}_5$, $\text{BrCH}_2(p\text{-C}_6\text{H}_4\text{CN})$, and $\text{BrCH}_2(p\text{-C}_6\text{H}_4\text{CF}_3)$, respectively, using a procedure similar to that of **2a**. Spectroscopic data for **2b** are as follows: ^1H NMR (CDCl_3) δ 7.62–6.84 (m, 25H, Ph), 3.56 (s, 3H, OCH₃), 3.27 (s, 2H, CH_2), 2.71 (m, 2PCH₂), 2.02 (m, PCH₂CH₂), 1.56 (s, 15H, 5CH₃); ^{31}P NMR (CDCl_3) δ 35.10; ^{13}C NMR (CDCl_3) δ 345.1 (t, C_α , $J_{\text{C-P}} = 14.0$ Hz), 171.5 (CO_2), 133.3–121.5 (Ph and C_β), 104.1 (Cp), 52.0 (OCH₃), 33.3 (CH_2), 29.1 (t, PCH₂, $J_{\text{C-P}} = 18.4$ Hz), 21.7 (PCH₂CH₂), 10.4 (5CH₃); MS (m/z , Ru^{102}) 823.3 ($\text{M}^+ - \text{Br}$), 750.2 ($\text{M}^+ - \text{Br} - \text{CH}_2\text{CO}_2\text{CH}_3$), 649.1 ($\text{M}^+ - \text{Br} - \text{CH}_2\text{CO}_2\text{CH}_3 - \text{CCPh}$). Anal. Calcd for $\text{C}_{48}\text{H}_{51}\text{O}_2\text{P}_2\text{BrRu}$: C, 63.85; H, 5.69. Found: C, 64.22; H, 5.83. Spectroscopic data for **2c** are as follows: ^1H NMR (CDCl_3) δ 7.44–6.76 (m, 25H, Ph), 3.97 (s, 2H, CH_2), 2.80 (m, 2PCH₂), 2.65 (m, PCH₂CH₂), 1.59 (s, 15H, 5CH₃); ^{31}P NMR (CDCl_3) δ 35.86; ^{13}C NMR (CDCl_3) δ 341.8 (t, C_α , $J_{\text{C-P}} = 14.5$ Hz), 134.1–123.7 (Ph), 119.4 (C_β), 104.2 (Cp), 29.1 (t, PCH₂, $J_{\text{C-P}} = 18.8$ Hz), 21.8 (PCH₂CH₂), 20.1 ($\text{CH}_2\text{C}_6\text{F}_5$), 10.5 (5CH₃); MS (m/z , Ru^{102}) 931 ($\text{M}^+ - \text{Br}$), 750.2 ($\text{M}^+ - \text{Br} - \text{CH}_2\text{C}_6\text{F}_5$), 649.1 ($\text{M}^+ - \text{Br} - \text{CH}_2\text{C}_6\text{F}_5 - \text{CCPh}$). Anal. Calcd for $\text{C}_{52}\text{H}_{48}\text{F}_5\text{P}_2\text{BrRu}$: C, 61.78; H, 4.79. Found: C, 62.35; H, 4.93. Spectroscopic data for **2d** are as follows: ^1H NMR (CDCl_3) δ 7.90–6.86 (m, 25H, Ph), 3.82 (s, 2H, CH_2), 2.70 (m, 2PCH₂), 2.17 (m, PCH₂CH₂), 1.63 (s, 15H, 5CH₃); ^{31}P NMR (CDCl_3) δ 35.77; ^{13}C NMR (CDCl_3) δ 345.4 (t, C_α , $J_{\text{C-P}} = 10.1$ Hz), 137.7–125.7 (Ph and C_β), 103.7 (Cp), 32.7 ($\text{CH}_2\text{C}_6\text{H}_5$), 29.2 (t, PCH₂, $J_{\text{C-P}} = 19.2$ Hz), 21.9 (PCH₂CH₂), 10.7 (5CH₃); MS (m/z , Ru^{102}) 841.4 ($\text{M}^+ - \text{Br}$), 750.2 ($\text{M}^+ - \text{Br} - \text{CH}_2\text{C}_6\text{H}_5$), 649.1 ($\text{M}^+ - \text{Br} - \text{CH}_2\text{C}_6\text{H}_5 - \text{CCPh}$). Anal. Calcd for $\text{C}_{52}\text{H}_{53}\text{P}_2\text{RuBr}$: C, 67.82; H, 5.80. Found: C, 68.25; H, 5.93. Spectroscopic data for **2e** are as follows: ^1H NMR (CDCl_3) δ 7.62–6.79 (m, 25H, Ph), 3.94 (s, 2H, CH_2), 2.77 (m, 2PCH₂), 2.13 (m, PCH₂CH₂), 1.59 (s, 15H, 5CH₃); ^{31}P NMR (CDCl_3) δ 35.46; ^{13}C NMR (CDCl_3) δ 344.6 (t, C_α , $J_{\text{C-P}} = 14.1$ Hz), 134.1–124.8 (Ph), 119.2 (C_β), 118.7 (CN), 103.8 (Cp), 29.2 (t, PCH₂, $J_{\text{C-P}} = 18.9$ Hz), 21.8

(PCH₂CH₂), 32.6 ($\text{CH}_2\text{C}_6\text{H}_4\text{CN}$), 10.6 (5CH₃); MS (m/z , Ru^{102}) 946.2 ($\text{M}^+ - \text{Br}$), 750.2 ($\text{M}^+ - \text{Br} - \text{CH}_2\text{C}_6\text{H}_4\text{CN}$), 649.1 ($\text{M}^+ - \text{Br} - \text{CH}_2\text{C}_6\text{H}_4\text{CN} - \text{CCPh}$). Anal. Calcd for $\text{C}_{53}\text{H}_{52}\text{NP}_2\text{RuBr}$: C, 67.30; H, 5.54; N, 1.48. Found: C, 68.35; H, 5.67; N, 1.35. Spectroscopic data for **2f** are as follows: ^1H NMR (CDCl_3) δ 7.59–6.83 (m, 25H, Ph), 3.89 (s, 2H, CH_2), 2.77 (m, 2PCH₂), 2.05 (m, PCH₂CH₂), 1.61 (s, 15H, 5CH₃); ^{31}P NMR (CDCl_3) δ 35.61; ^{13}C NMR (CDCl_3) δ 345.0 (t, C_α , $J_{\text{C-P}} = 16.3$ Hz), 142.5–125.1 (Ph and C_β), 103.8 (Cp), 32.4 ($\text{CH}_2\text{C}_6\text{H}_4\text{CN}$), 29.2 (t, PCH₂, $J_{\text{C-P}} = 19.5$ Hz), 21.9 (PCH₂CH₂), 10.6 (5CH₃); MS (m/z , Ru^{102}) 989.2 ($\text{M}^+ - \text{Br}$), 750.2 ($\text{M}^+ - \text{Br} - \text{CH}_2\text{C}_6\text{H}_4\text{CF}_3$), 649.1 ($\text{M}^+ - \text{Br} - \text{CH}_2\text{C}_6\text{H}_4\text{CF}_3 - \text{CCPh}$). Anal. Calcd for $\text{C}_{53}\text{H}_{52}\text{F}_3\text{P}_2\text{RuBr}$: C, 64.37; H, 5.30. Found: C, 64.58; H, 5.49.

Synthesis of $[\text{Ru}]\text{C}\equiv\text{C}(\text{Ph})\text{CHCN}$ (3a**).** To a 15 mL acetonitrile solution of complex **2a** (1.70 g, 1.854 mmol) was added an aliquot of *n*Bu₄NOH (1 M in MeOH, 2 mL). The mixture was stirred at room temperature for 30 min to give bright yellow precipitates. The precipitate was filtered and washed with 2 \times 10 mL of acetonitrile and dried under vacuum to give the product **3a** (1.33 g, 91% yield). Spectroscopic data for **3a** are as follows: ^1H NMR (CDCl_3) δ 7.72–7.03 (m, 25H, Ph), 2.65 (m, 2PCH₂), 1.93 (m, PCH₂CH₂), 1.35 (s, 15H, 5CH₃), 1.07 (s, 1H, CH); ^{31}P NMR (CDCl_3) δ 48.13, 45.52 (AB, $J_{\text{P-P}} = 49.76$ Hz); ^{13}C NMR (CDCl_3) δ 135.2–122.7 (Ph and C_β), 134.0 (t, C_α , $J_{\text{C-P}} = 5.74$ Hz), 114.0 (CN), 94.0 (Cp), 29.9 (t, PCH₂, $J_{\text{C-P}} = 28.1$ Hz), 24.1 (PCH₂CH₂), 13.7 (CH), 10.0 (5CH₃); MS (m/z , Ru^{102}) 790.1 ($\text{M}^+ + 1$), 751.2 ($\text{M}^+ - \text{CHCN}$), 649.1 ($\text{M}^+ - \text{CHCN} - \text{CCPh}$). Anal. Calcd for $\text{C}_{47}\text{H}_{47}\text{NP}_2\text{Ru}$: C, 71.55; H, 6.01; N, 1.78. Found: C, 72.31; H, 6.37; N, 1.55.

Synthesis of $[\text{Ru}]\text{C}\equiv\text{C}(\text{Ph})\text{CH}(\text{CO}_2\text{CH}_3)$ (3b**).** To a 10 mL acetone solution of complex **2b** (500 mg, 0.554 mmol) was added an aliquot of (*n*Bu)₄NOH (1 M in MeOH, 1.0 mL). The mixture was stirred at room temperature for 30 min to give bright yellow precipitates, which were filtered and washed with 2 \times 5 mL of acetone, then dried under vacuum to give the product **3b** (340 mg, 77% yield). Spectroscopic data for **3b** are as follows: ^1H NMR (CDCl_3) δ 7.63–6.89 (m, 25H, Ph), 3.43 (s, 3H, OCH₃), 2.43 (m, 4H, PCH₂), 2.02 (m, PCH₂CH₂), 1.60 (s, 1H, CH), 1.34 (s, 15H, 5CH₃); ^{31}P NMR (CDCl_3) δ 47.73, 43.00 (AB, $J_{\text{P-P}} = 50.18$ Hz); ^{13}C NMR (CDCl_3) δ 183.6 (CO_2), 134.0–119.4 (Ph and C_α), 104.2 (C_β), 89.1 (Cp), 52.1 (OCH₃), 26.8 (t, $J_{\text{C-P}} = 13.7$ Hz, PCH₂), 21.5 (PCH₂CH₂), 10.0 (CH), 10.5 (5CH₃), 9.7 (CH); MS (m/z , Ru^{102}) 823.1 ($\text{M}^+ + 1$), 750.2 ($\text{M}^+ - \text{CHCO}_2\text{CH}_3$), 649.1 ($\text{M}^+ - \text{CHCO}_2\text{CH}_3 - \text{CCPh}$). Anal. Calcd for $\text{C}_{48}\text{H}_{50}\text{O}_2\text{P}_2\text{Ru}$: C, 70.14; H, 6.13. Found: C, 71.23; H, 6.37.

Synthesis of $[\text{Ru}]\text{C}\equiv\text{C}(\text{Ph})\text{CH}(\text{CN})\text{C}(\text{CH}_3)_2\text{O}$ (4**).** To a 15 mL acetone solution of **2a** (500 mg, 0.634 mmol) was added an aliquot of *n*Bu₄NOH (1 M in MeOH, 1.0 mL). The mixture was stirred at room temperature for 5 min to give a bright yellow solution of **3a**. The solution was stirred at room temperature for 5 days, and then the solvent was reduced to 2 mL under vacuum. To the residue, 30 mL of MeOH was added, and yellow precipitates thus formed were filtered and washed with 2 \times 5 mL of MeOH. The ^{31}P NMR spectrum indicates the presence of two products in a ratio of 2:1. Thus the product was passed through a silica gel-packed column eluted with 1:1 ethyl acetate/hexane, and only a yellow band was collected. After the solvent was removed under vacuum the yellow band gave a single product, **4** (280 mg, 52% yield). The minor product decomposed in the column. Spectroscopic data for **4** are as follows: ^1H NMR (CDCl_3) δ 7.58–6.17 (m, 25H, Ph), 2.86 (t, PCH₂, $J_{\text{H-P}} = 9.85$ Hz), 2.54 (m, PCH₂CH₂), 2.86 (t, PCH₂, $J_{\text{H-P}} = 13.57$ Hz), 1.57 (s, 1H, CH), 1.22 (s, 6H, 2CH₃), 1.08 (s, 15H, 5CH₃); ^{31}P NMR (CDCl_3) δ 45.43, 39.11 (AB, $J_{\text{P-P}} = 52.21$ Hz); ^{13}C NMR (CDCl_3) δ 145.2 (O(CCH₃)₂), 135.1–123.6 (Ph, C_α and C_β), 113.1 (CN), 93.3 (Cp), 31.9 (t, PCH₂, $J_{\text{C-P}} = 18.7$ Hz), 22.1 (PCH₂), 9.6 (CH), 10.4 (5CH₃); MS (m/z , Ru^{102}) 848.3 ($\text{M}^+ + 1$), 790.2 ($\text{M}^+ - \text{CH}_3\text{COCH}_3$), 751.2

(41) Oshima, N.; Suzuki, H.; Moro-oka, Y. *Chem. Lett.* **1984**, 1161.

($M^+ - CH_3COCH_3 - CHCN$), 649.1 ($M^+ - CH_3COCH_3 - CHCN - CCPh$). Anal. Calcd for $C_{50}H_{53}NOP_2Ru$: C, 70.90; H, 6.31; N, 1.65. Found: C, 71.33; H, 6.45; N, 1.65. ^{31}P NMR data of the minor product **4'**: ^{31}P NMR ($CDCl_3$) δ 28.67, 11.77 ($J_{P-P} = 50.23$ Hz).

Synthesis of $[[Ru]=CC(Ph)(CH_2CN)CH(CN)C(CH_3)_2O][I]$ (5a**).** A Schlenk flask was charged with ICH_2CN (520 μL , 0.590 mmol) and **4** (100 mg, 0.118 mmol) in 10 mL of CH_2Cl_2 . The mixture was stirred at room temperature for 8 h. The solvent was reduced to about 2 mL under vacuum, and the residue was added to 20 mL of vigorously stirred diethyl ether. The brown powder thus formed was filtered and washed with 2×5 mL of diethyl ether and dried under vacuum to give the product **5a** (98.5 mg, 82% yield). Spectroscopic data for **5a** are as follows: 1H NMR ($CDCl_3$) δ 7.74–6.18 (m, 25H, Ph), 5.28 (s, 2H, CH_2), 2.84 (m, 2H, CH_2), 2.59, 2.13 (m, 2H, PCH_2), 1.46 (s, 1H, CHCN), 1.14 (s, 6H, $2CH_3$), 1.17 (s, 15H, $5CH_3$); ^{31}P NMR ($CDCl_3$) δ 37.30, 31.45 (AB, $J_{P-P} = 48.02$ Hz); ^{13}C NMR ($CDCl_3$) δ 290.6 (t, C_α , $J_{C-P} = 11.6$ Hz), 139.0–127.7 (Ph), 116.1, 115.2 (CN), 102.0 (Cp), 97.5 ($OC(CH_3)_2$), 70.0 (CH_2), 28.8 (dd, $J_{C-P} = 29.9$, 6.4 Hz, PCH_2), 27.6 (dd, $J_{C-P} = 30.7$, 5.3 Hz, PCH_2), 22.6, 21.1 ($2CH_3$), 20.4 (CH_2), 14.0 (s, CHCN), 10.3 ($5CH_3$); MS (m/z , Ru^{102}) 887.3 ($M^+ - I$), 649.1 ($M^+ - I - CH_3COCH_3 - CHCN - CCPh - CH_2CN$). Anal. Calcd for $C_{52}H_{55}N_2OP_2Ru$: C, 61.60; H, 5.47; N, 2.76. Found: C, 62.03; H, 5.64; N, 2.42.

Complex $[[Ru]=C-C(Ph)(CH_2CO_2CH_3)CH(CN)C(CH_3)_2O][Br]$ (5b**)** (100 mg, 88% yield) was prepared from **4** (100 mg, 0.118 mmol) with $BrCH_2CO_2CH_3$ (56 μL , 0.590 mmol) using a procedure similar to that of **5a**. Spectroscopic data of **5b** are as follows: 1H NMR (CD_3COCD_3) δ 7.77–6.18 (m, 25H, Ph), 3.81 (s, 2H, CH_2), 3.76 (s, 3H, OCH_3), 3.34 (t, 2H, $J_{H-H} = 13.42$ Hz, PCH_2), 2.95 (m, 2H, PCH_2CH_2), 2.18 (t, 2H, $J_{H-H} = 13.42$ Hz, PCH_2), 1.79 (s, 6H, $2CH_3$), 1.59 (s, 1H, CH), 1.17 (s, 15H, $5CH_3$); ^{31}P NMR ($CDCl_3$) δ 37.38, 31.94 ($J_{P-P} = 52.91$ Hz); ^{13}C NMR ($CDCl_3$) δ 291.1 (t, C_α , $J_{C-P} = 12.2$ Hz), 167.7 (CO_2), 139.1–127.7 (Ph), 119.4 (C_β), 115.3 (CN), 102.0 (Cp), 97.4 ($OC(CH_3)_2$), 70.3 (CH_2), 28.9 (dd, $J_{C-P} = 30.8$, 5.5 Hz, PCH_2), 27.3 (dd, $J_{C-P} = 29.1$, 6.0 Hz, PCH_2), 21.1 (PCH_2CH_2), 20.5 ($2CH_3$), 13.7 (CHCN), 10.2 ($5CH_3$); MS (m/z , Ru^{102}) 920.3 ($M^+ - Br$), 649.1 ($M^+ - Br - CH_3COCH_3 - CHCN - CCPh - CH_2CO_2CH_3$). Anal. Calcd for $C_{53}H_{58}NO_3P_2RuBr$: C, 63.66; H, 5.85; N, 1.40. Found: C, 64.18; H, 6.01; N, 1.23.

Synthesis of $[[Ru]=CC(Ph)=C(CN)C(CH_3)_2O][I]$ (6**).** A Schlenk flask was charged with ICH_2CN (510 μL , 0.590 mmol) and **4** (100 mg, 0.118 mmol) and 10 mL of CH_2Cl_2 . The mixture was heated to reflux for 24 h. Then the solvent was reduced to about 2 mL under vacuum, and the residue was added to 20 mL of vigorously stirred *n*-hexane. The brown powders thus formed were filtered and washed with 2×5 mL of diethyl ether and dried under vacuum to give **6** (75 mg, 65% yield). Spectroscopic data for **6** are as follows: 1H NMR ($CDCl_3$) δ 7.71–6.18 (m, 25H, Ph), 2.84 (t, 2H, $J_{H-H} = 14.15$ Hz, PCH_2CH_2), 2.62, 2.08 (2m, 4H, PCH_2), 1.14 (s, 6H, $2CH_3$), 1.06 (s, 15H, $5CH_3$); ^{31}P NMR ($CDCl_3$) δ 36.78. ^{13}C NMR ($CDCl_3$) δ 275.0 (t, C_α , $J_{C-P} = 12.2$ Hz), 163.0 (C_β), 139.6–128.9 (Ph), 120.6 (C_γ), 114.1 (CN), 103.5 (Cp), 102.1 ($OC(CH_3)_2$), 29.1 (t, $J_{C-P} = 18.3$ Hz, PCH_2), 22.3 (PCH_2CH_2), 12.1 ($5CH_3$), 11.5 ($2CH_3$); MS (m/z , Ru^{102}) 846.2 ($M^+ - I$), 649.1 ($M^+ - I - CH_3COCH_3 - CCN - CCPh$). Anal. Calcd for $C_{50}H_{52}NOP_2IRu$: C, 61.73; H, 5.39; N, 1.44. Found: C, 62.17; H, 5.52; N, 1.17.

Synthesis of $[[Ru]=CCH(Ph)CH(CN)C(CH_3)_2O][CF_3COO]$ (7**).** A Schlenk flask was charged with CF_3COOH (95 μL , 1.18 mmol) and **4** (100 mg, 0.118 mmol) in 10 mL of CH_2Cl_2 . The mixture was stirred at room temperature for 1 h. The solvent was reduced to about 2 mL under vacuum, and 20 mL of diethyl ether was added to the residue. The brown powder thus formed was filtered and washed with 2×5 mL of diethyl ether and dried under vacuum to give **7** (85 mg, 75% yield).

Spectroscopic data for **7** are as follows: 1H NMR (CD_3COCD_3) δ 7.63–6.16 (m, 25H, Ph), 5.13 (s, 1H, $CHPh$), 3.20 (t, 1H, $J_{H-P} = 10.19$ Hz, CH_2), 2.93 (t, 1H, $J_{H-P} = 13.14$ Hz, CH_2), 2.82–2.45 (m, 2H, PCH_2), 2.19–2.08 (m, 2H, PCH_2), 1.59 (s, 1H, CHCN), 1.24, 1.09 (s, 3H, $2CH_3$), 1.15 (s, 15H, $5CH_3$); ^{31}P NMR ($CDCl_3$) δ 38.63, 32.97 (2d, $J_{P-P} = 48.03$ Hz); ^{13}C NMR ($CDCl_3$) δ 290.5 (t, $J_{C-P} = 12.7$ Hz, C_α), 138.2–128.3 (Ph and C_β), 116.3 (CN), 102.2 (Cp), 97.3 ($OC(CH_3)_2$), 70.2 ($CHPh$), 30.7, 30.2 ($2CH_3$), 28.7 (dd, $J_{C-P} = 28.6$, 6.0 Hz, PCH_2), 28.3 (dd, $J_{C-P} = 28.6$, 5.8 Hz, PCH_2), 27.8 (CHCN), 20.3 (PCH_2CH_2), 10.1 ($5CH_3$); MS (m/z , Ru^{102}) 849.3 ($M^+ - CF_3COO$), 649.1 ($M^+ - CH_3COCH_3 - CHCN - CCPh - H$). Anal. Calcd for $C_{52}H_{54}NO_3F_3P_2Ru$: C, 64.99; H, 5.39; N, 1.44. Found: C, 65.38; H, 5.61; N, 1.25.

Synthesis of $[[Ru]=CC(Ph)(HgCl)CH(CN)C(CH_3)_2O][Cl]$ (8**).** A Schlenk flask was charged with $HgCl_2$ (160 mg, 0.59 mmol) and **4** (100 mg, 0.118 mmol) in 10 mL of CH_2Cl_2 . The mixture was stirred at room temperature for 30 min. Excess $HgCl_2$ was filtered, and the solvent was reduced to about 2 mL under vacuum. The residue was added to a 20 mL solution of vigorously stirred diethyl ether. The black-blue powder thus formed was filtered and washed with 2×5 mL of diethyl ether and dried under vacuum to give **8** (115 mg, 90% yield). Spectroscopic data for **8** are as follows: 1H NMR (CD_3COCD_3) δ 7.67–6.92 (m, 25H, Ph), 3.20 (s, 1H, CHCN), 2.43 (m, 2H, PCH_2CH_2), 2.00 (t, 2H, $J_{H-P} = 15.80$ Hz, PCH_2), 1.80 (t, 2H, $J_{H-P} = 13.80$ Hz, PCH_2), 1.61 (s, 6H, $2CH_3$), 1.21 (s, 15H, $5CH_3$); ^{31}P NMR ($CDCl_3$) δ 37.83, 32.23 ($J_{P-P} = 50.85$ Hz); ^{13}C NMR ($CDCl_3$) δ 309.7 (t, $J_{C-P} = 14.6$ Hz, C_α), 137.3–125.1 (Ph and C_β), 118.5 (CN), 92.5 (Cp), 89.2 ($OC(CH_3)_2$), 30.7 (t, $J_{C-P} = 23.1$ Hz, $2PCH_2$), 27.8, 27.4 ($2CH_3$), 21.4 (PCH_2CH_2), 10.3 (CHCN), 9.3 ($5CH_3$); MS (m/z , Ru^{102} , Hg^{202}) 1049.3 ($M^+ - Cl$), 649.1 ($M^+ - Cl - CH_3COCH_3 - CHCN - HgCl - CCPh$). Anal. Calcd for $C_{50}H_{53}Cl_2P_2RuHg$: C, 55.17; H, 4.91. Found: C, 56.33; H, 5.02.

Synthesis of $[[Ru]=C=C(Ph)CH(CN)(HgCl)][Cl]$ (9**).** A Schlenk flask was charged with $HgCl_2$ (170 mg, 0.634 mmol) and **3a** (100 mg, 0.127 mmol) in 10 mL of CH_2Cl_2 . The mixture was stirred at room temperature for 30 min. Excess $HgCl_2$ was filtered, and the solvent was reduced to about 2 mL under vacuum. The residue was added to a 20 mL solution of vigorously stirred diethyl ether. The pink powder thus formed was filtered and washed with 2×5 mL of diethyl ether and dried under vacuum to give **9** (116 mg, 86% yield). Spectroscopic data for **9** are as follows: 1H NMR ($CDCl_3$) δ 7.84–6.54 (m, 25H, Ph), 3.66 (s, 1H, CH), 2.95 (m, 2H, PCH_2), 2.81 (m, 2H, PCH_2), 2.70 (m, 2H, PCH_2CH_2), 1.59 (s, 15H, $5CH_3$); ^{31}P NMR ($CDCl_3$) δ 37.88, 32.82 (2d, $J_{P-P} = 50.39$ Hz); ^{13}C NMR ($CDCl_3$) δ 340.7 (t, $J_{C-P} = 14.6$ Hz, C_α), 134.1–128.0 (Ph and C_β), 122.1 (CN), 104.6 (Cp), 31.2 (d, $J_{C-P} = 35.3$ Hz, PCH_2), 29.9 (CH), 28.7 (d, $J_{C-P} = 32.9$ Hz, PCH_2), 21.8 (PCH_2CH_2), 10.6 ($5CH_3$); MS (m/z , Ru^{102} , Hg^{202}) 991.3 ($M^+ - Cl$), 649.1 ($M^+ - Cl - CHCN - HgCl - CCPh$). Anal. Calcd for $C_{47}H_{47}NP_2Cl_2RuHg$: C, 52.23; H, 4.47; N, 1.32. Found: C, 52.55; H, 4.75; N, 1.20.

Synthesis of $[Ru]N_3$ (10**).** A Schlenk flask was charged with $(CH_3)_3SiN_3$ (78 μL , 0.590 mmol) and **3a** (100 mg, 0.127 mmol) and 10 mL of THF. The mixture was stirred at room temperature for 3 h. The solvent was reduced to about 2 mL under vacuum and added to 20 mL of vigorously stirred *n*-hexane. The yellow powder thus formed was filtered and washed with 2×5 mL of *n*-hexane and dried under vacuum to give the product **10** (68 mg, 78% yield). Spectroscopic data for **10** are as follows: 1H NMR ($CDCl_3$) δ 7.65–6.94 (m, 25H, Ph), 2.56 (t, 4H, $J_{H-P} = 13.33$ Hz, PCH_2), 2.31 (m, 2H, PCH_2CH_2), 1.37 (s, 15H, $5CH_3$); ^{31}P NMR ($CDCl_3$) δ 38.26. ^{13}C NMR ($CDCl_3$) δ 138.6–127.5 (Ph, C_α and C_β), 89.6 (Cp), 27.9 (t, $J_{C-P} = 13.8$ Hz, PCH_2), 21.2 (PCH_2CH_2), 9.6 ($5CH_3$); MS (m/z , Ru^{102}) 692.3 ($M^+ + 1$), 675.3 ($M^+ - N - 1$), 649.3 ($M^+ -$

Table 6. Crystal and Intensity Collection Data for (C₅Me₅)(dppp)RuC≡C(Ph)CHCN (3a), (C₅Me₅)(dppp)RuC≡C(Ph)CH(CN)C(CH₃)₂O (4), [(C₅Me₅)(dppp)Ru=C(C(Ph)=C(CN)C(CH₃)₂O)][I]·2CHCl₃ (6), [(C₅Me₅)(dppp)Ru=CCH(Ph)CH(CN)C(CH₃)₂O][CF₃COO]·1/2CF₃COOH (7), and [(C₅Me₅)(dppp)RuNCCH₂I][I₃] (11)

	C ₄₇ H ₄₇ NP ₂ Ru, 3a	C ₅₀ H ₅₃ NOPRu, 4	C ₅₂ H ₅₃ Cl ₆ INOP ₂ Ru, 6	C ₅₄ H _{55.5} Cl ₃ F _{4.5} NO ₄ P ₂ Ru, 7	C ₃₉ H ₄₃ I ₄ NP ₂ Ru, 11
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
cryst syst	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic
<i>a</i> , Å	16.1153(3)	11.2771(3)	21.4873(4)	12.1587(5)	15.5340(1)
<i>b</i> , Å	12.2925(1)	17.8994(4)	13.2421(3)	19.1984(8)	13.2322(1)
<i>c</i> , Å	19.9973(4)	23.8595(5)	19.5952(4)	24.7050(9)	21.3003(2)
α , deg	90	90	90	69.400(1)	90
β , deg	95.010(1)	90	105.965(1)	76.820(1)	103.684(1)
γ , deg	90	90	90	89.762(1)	90
<i>V</i> , Å ³	3946.28(11)	4816.1(2)	5360.5(2)	5237(6)	4253.98(6)
<i>Z</i>	4	4	4	4	4
cryst dims, mm	0.40 × 0.22 × 0.18	0.35 × 0.15 × 0.12	0.35 × 0.30 × 0.05	0.20 × 0.18 × 0.04	0.36 × 0.34 × 0.05
2 θ range, deg	1.56 to 27.50	1.42 to 26.37	1.83 to 26.37	0.91 to 25.00	1.35 to 26.40
total no. of reflns	9047	9796	10 542	17 577	8552
final <i>R</i> indices	<i>R</i> 1 = 0.0279, [<i>I</i> > 2 σ (<i>I</i>)] w <i>R</i> 2 = 0.0715	<i>R</i> 1 = 0.0702, w <i>R</i> 2 = 0.1702	<i>R</i> 1 = 0.0542, w <i>R</i> 2 = 0.1282	<i>R</i> 1 = 0.0964, w <i>R</i> 2 = 0.1848	<i>R</i> 1 = 0.0491, w <i>R</i> 2 = 0.1162
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0394, w <i>R</i> 2 = 0.0779	<i>R</i> 1 = 0.1166, w <i>R</i> 2 = 0.1928	<i>R</i> 1 = 0.0945, w <i>R</i> 2 = 0.1456	<i>R</i> 1 = 0.1487, w <i>R</i> 2 = 0.2080	<i>R</i> 1 = 0.0593, w <i>R</i> 2 = 0.1245

N₃). Anal. Calcd for C₃₇H₄₁N₃P₂Ru: C, 64.33; H, 5.98; N, 6.08. Found: C, 64.46; H, 6.10; N, 5.93.

Synthesis of [(Ru)NCCH₂I][I₃] (11). A Schlenk flask was charged with ICH₂CN (100 μ L, 1.45 mmol) and **10** (100 mg, 0.145 mmol) in 10 mL of CH₂Cl₂. The mixture was stirred at room temperature for 3 h. The solvent was reduced to about 2 mL under vacuum and added to 20 mL of vigorously stirred *n*-pentane. The orange-yellow powder thus formed was filtered and washed with 5 mL of *n*-pentane and dried under vacuum to give **11** (66 mg, 56% yield). Spectroscopic data for **11** are as follows: ¹H NMR (CDCl₃) δ 8.07–6.83 (m, 25H, Ph), 4.50 (s, 2H, CH₂), 2.59 (m, 2H, PCH₂), 2.43 (m, 2H, PCH₂CH₂), 2.00 (m, 2H, PCH₂), 1.54 (s, 15H, 5CH₃); ³¹P NMR (CDCl₃) δ 35.01; ¹³C NMR (CDCl₃) δ 133.8–124.7 (Ph, C _{α} and C _{β}), 119.4 (CN), 93.2 (Cp), 50.9 (CH₂), 29.4 (t, *J*_{C–P} = 8.22 Hz, PCH₂), 20.3 (PCH₂CH₂), 9.7 (5CH₃); MS (*m/z*, Ru¹⁰²) 816.2 (M⁺ + 1 – I₃), 776.1 (M⁺ – I₃ – CH₂CN), 649.3 (M⁺ – I₄ – CH₂CN). Anal. Calcd for C₃₉H₄₂NP₂RuI₄: C, 39.18; H, 3.54; N, 1.17. Found: C, 40.25; H, 3.73; N, 1.06.

X-ray Analysis of 3a. Single crystals of **3a** suitable for X-ray diffraction study were grown as mentioned above. A single crystal of dimensions 0.32 × 0.08 × 0.05 mm³ was glued to a glass fiber and mounted on a 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.⁴² SADABS⁴³ (Siemens area detector absorption) absorption correction was applied, and decay was negligible. Data were

processed and the structures were solved and refined by the SHELXTL⁴⁴ program. The structure was solved using direct methods and confirmed by Patterson methods refining on intensities of all data (20 610 reflections) to give w*R*1 = 0.0579 and w*R*2 = 0.1221⁴⁵ for 20 610 unique observed reflections (*I* > 2 σ (*I*)). Hydrogen atoms were placed geometrically using the riding model, with thermal parameters set to 1.2 times that for the atoms to which the hydrogen is attached and 1.5 times that for the methyl hydrogens. The procedures for the structure determination of **4**, **6**, **7**, and **11** were similar to that of **3a**. Crystal data of these complexes are listed in Table 6.

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Supporting Information Available: Details of the structural determination for complexes **3a**, **4**, **6**, **7**, and **11** including crystal and intensity collection data, positional and anisotropic thermal parameters, and all of the bond distances and angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM000094L

(44) SHELXTL: Structure Analysis Program, version 5.04; Siemens Industrial Automation Inc.: Madison, WI, 1995.

(45) GOF = $[\sum(w(F_o^2 - F_c^2)^2)/(n - p)]^{1/2}$, where *n* and *p* denote the number of data and parameters. *R*1 = $(\sum||F_o| - |F_c||)/\sum|F_o|$, w*R*2 = $[\sum(w(F_o^2 - F_c^2)^2)/\sum(w(F_o^2)^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [(max; 0, F_o^2) + 2F_c^2]/3$.

(42) SAINT (Siemens Area Detector Integration) program; Siemens Analytical X-ray: Madison, WI, 1995.

(43) The SADABS program is based on the method of Blessing; see: Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.