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 [Ru]-C=C(Ph)CHR ([Ru] = (η^5-C_5Me_5)(dppp)Ru, dppp = $Ph_2PCH_2CH_2CH_2PPh_2$, R = CN, **3a**; R = CO_2CH_3, **3b**). Insertion of acetone into the three-membered ring of **3a** gave the neutral dihydrofuranyl complex [Ru]-C=C(Ph)CH(CN)CMe_2O (**4**). Electrophilic addition at C_β of **4** afforded cationic carbene complexes [[Ru]=CC(R′)(Ph)CH(CN)C$(CH_3)_2$O]$^+$ (R′ = CH_2CN, **5a**; R′ = $CH_2CO_2CH_3$, **5b**; R′ = H, **7**; R′ = HgCl, **8**). Complexes **5a** and **5b** transformed to [[Ru]=CC(Ph)=C(CN)C$(CH_3)_2$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 [Ru]N_3 with ICH_2CN gave [Ru]-NCH_2I (**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, [Cp$(PPh_3)_2$Ru=C=C(Ph)-CH_2CN]$^+$ was found to undergo deprotonation to afford the cyclopropenyl complex Cp$(PPh_3)_2$RuC=C(Ph)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 cyclopropenylium complex by loss of methanol. In our study, we also noticed that replacement of the Cp ligand with a Tp ligand[23] makes one of the phosphines labile, and a facile substitution reaction was observed for Tp ruthenium cyclopropenyl complexes. To extend the breadth, we

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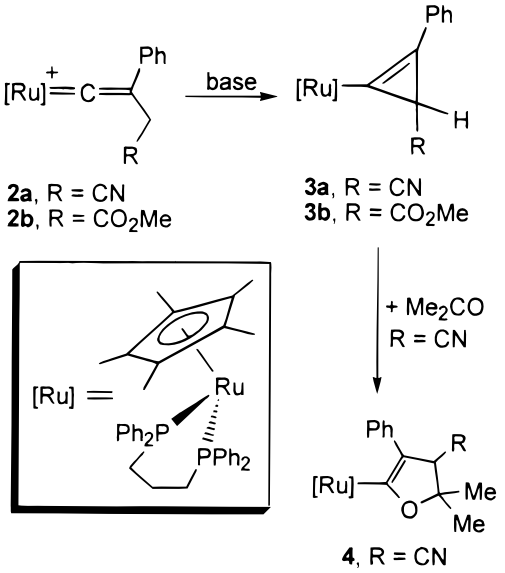
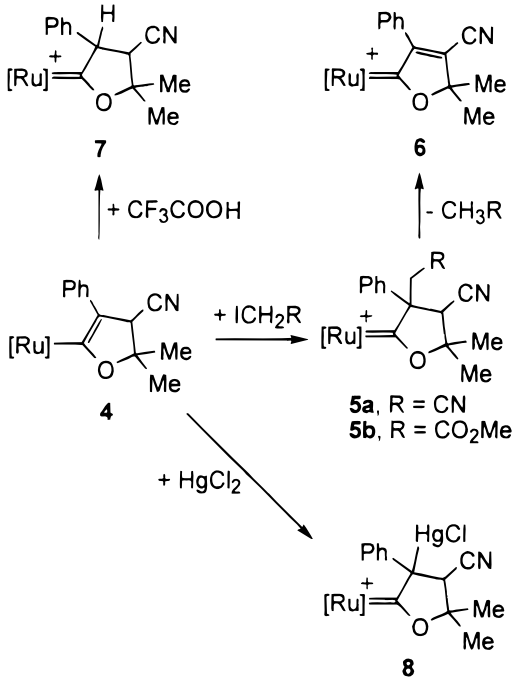
Scheme 1



Scheme 2



have explored the effect of C_5Me_5 (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* = η^5-C_5Me_5, dppp = $Ph_2PCH_2CH_2CH_2PPh_2$) with ICH_2-CN in CH_2Cl_2 afforded the cationic vinylidene complex $[[Ru]{=}C{=}C(Ph)CH_2CN]^+$ (**2a**) in 85% yield (Scheme 1). Unlike other vinylidene complexes,[5] which are generally prepared at room temperature, **2a** is prepared by heating a CH_2Cl_2 solution of **1** and ICH_2CN 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 $[[Ru]{=}C{=}C(Ph)CH_2R]^+$ (R = CO_2CH_3, **2b**; R = C_6F_5, **2c**; R = C_6H_5, **2d**; R = *p*-C_6H_4-CN, **2e**; R = *p*-$C_6H_4CF_3$, **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 ^{13}C NMR spectra of these vinylidene complexes appear as triplets in the region of $\delta = 343 \pm 3$. The ^{31}P NMR resonance appears as a singlet at $\delta = 35 \pm 1$ in $CDCl_3$ at room temperature due to the fluxional behavior of the vinylidene ligand.[24,25]

Cyclopropenation of Vinylidene Complexes. Deprotonation of **2a** by *n*-Bu_4NOH 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*-Bu_4NF (1 M in THF), DBU (1,8-diazabicyclo[5.4.0]undecene), or KOH (dissolved in a minimum amount of H_2O) also gives **3a** in comparable 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 CH_2Cl_2, $CHCl_3$, THF, and benzene, slightly soluble in acetone and diethyl ether, but insoluble in *n*-hexane, CH_3CN, and MeOH. The ^{31}P NMR spectrum of **3a** displays two doublet resonances at δ 48.13 and 45.15 with $^2J_{P-P} = 49.76$ Hz in $CDCl_3$ 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 $^{13}C\{^1H\}$ 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)$CHCO_2CH_3$ (**3b**) in 77% yield. This reaction can only be carried out in acetone and only by using *n*-Bu_4NOH as a proton abstractor. Previously we reported that deprotonation of the analogous complex[22] $[(\eta^5\text{-}C_5H_5)(PPh_3)_2Ru{=}C{=}C(Ph)CH_2CO_2CH_3]^+$ 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 ^{31}P 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*-Bu_4NF, DBU, or KOH. Analogous Cp vinylidene complexes undergo a deprotonation reaction to yield cyclization products.[22] There-

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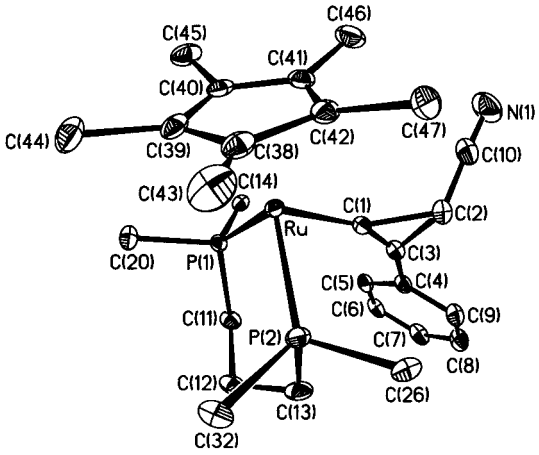

Figure 1. ORTEP drawing of **3a** with thermal ellipsoids shown at the 30% probability level. For phenyl groups on dppp, only the ipso carbons are shown.

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 cyclopropenylium 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 C(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 complex[38] 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 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.

Table 1. Selected Bond Distances (Å) and Angles (deg) of (η^5-C_5Me_5)(dppp)RuC=C(Ph)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)

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, [Ru]C=C(Ph)CH(CN)C(CH_3)$_2$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_{P-P} = 52.12 Hz are assigned to **4**. The ^{1}H 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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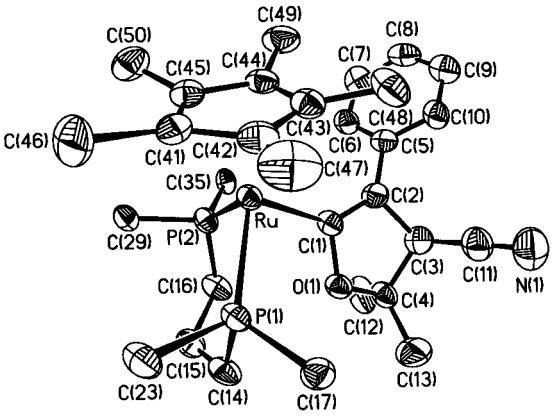


Figure 2. ORTEP drawing of **4** with thermal ellipsoids shown at the 30% probability level. For phenyl groups on dppp, only the ipso carbons are shown.

Table 2. Selected Bond Distances (Å) and Angles (deg) of (η^5-C_5Me_5)(dppp)RuC=C(Ph)CH(CN)C(CH_3)$_2$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*-Bu_4NOH. In these solvent systems, **3a** formed in good yield, but no insertion product was observed at room temperature. Addition of PhNCO, PhNCS, $(CF_3)_2CO$, 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 ^{31}P NMR spectrum of the mixture displaying two doublet ^{31}P 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(CH_3)$_2$ (**4′**) is speculated.

Electrophilic Additions of Ruthenium Cyclopentenyl Complex 4. Treatment of **4** with organic halides XCH_2R afforded cationic cyclic carbene complexes [[Ru]=CC(CH_2R)(Ph)CH(CN)C(CH_3)$_2$O][X] (R = CN, X = I, **5a**; R = CO_2CH_3, X = Br, **5b**) in high yields. Both ^{31}P 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 ^{31}P doublets, indicating high diastereoselectivity. 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 ^{13}C NMR spectrum.

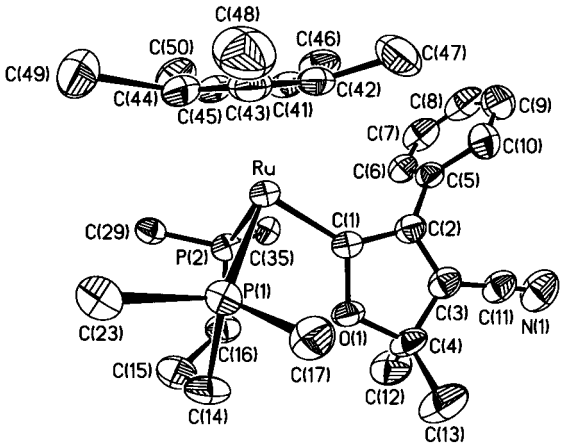


Figure 3. ORTEP drawing of **6** with thermal ellipsoids shown at the 30% probability level. For phenyl groups on dppp, only the ipso carbons are shown.

Table 3. Selected Bond Distances (Å) and Angles (deg) of (η^5-C_5Me_5)(dppp)Ru=CC(Ph)=C(CN)C(CH_3)$_2$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)		

Elimination of CH_3CN from **5a** in $CDCl_3$ generated the new cationic cyclic carbene complex [[Ru]=CC(Ph)=C(CN)C(CH_3)$_2$O][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 $CHCl_3$ after 1 day. Complex **6** can also be obtained directly by thermolysis of **4** in the presence ICH_2CN or $BrCH_2CO_2CH_3$. The ^{31}P NMR spectrum of **6** displays a singlet at δ 37.1, and, in the ^{13}C 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 $C(sp^2)$−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 sp^2 hybridization for C2 and C3.

Protonation of **4** with CF_3COOH occurs also at C_β of the five-membered ring, yielding the carbene complex [[Ru]=CCH(Ph)CH(CN)C$(CH_3)_2$O][CF_3COO] (**7**) (Scheme 2). This reaction is faster compared to the reaction of **4** with XCH_2R (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 ^{31}P 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 ^{13}C 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 ($M^+ - CF_3COO$). In solution, **7** slowly transformed to **6** by elimination of H_2. 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 $HgCl_2$ to **4** resulted in immediate formation of the blue carbene complex [[Ru]=CC(HgCl)(Ph)-CH(CN)C$(CH_3)_2$O][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 ^{31}P NMR spectrum. The minor isomer escaped from purification by recrystallization again, since only the major one was obtained. The ^{13}C NMR spectrum of the major isomer of **8** consists of strongly deshielded C_α resonance as a triplet at δ 309.7 in $CDCl_3$ at room temperature. No transformation of **8** to **6** is observed in $CDCl_3$ 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 sp^2 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 angle (108°). Formation of carbene complexes **5**, **7**, and **8** occurs by selective addition of electrophile (XCH_2R, H^+, and $HgCl_2$) to the nucleophilic C_β of the five-membered ring in **4**. Possibly because of steric crowding around C_β and C_γ, it is inclined to form a more stable carbene complex **6** by elimination of a small molecule.

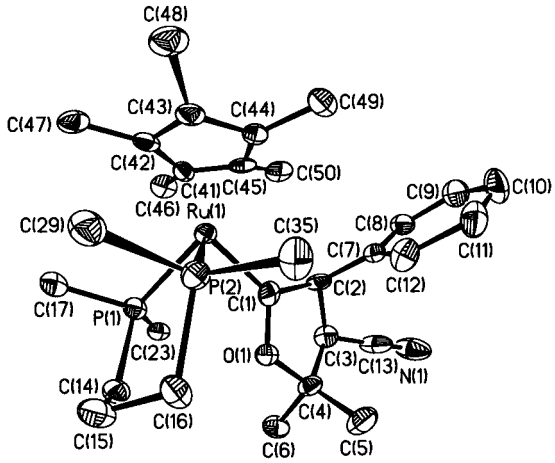


Figure 4. ORTEP drawing of **7** with thermal ellipsoids shown at the 30% probability level. For phenyl groups on dppp, only the ipso carbons are shown.

Table 4. Selected Bond Distances (Å) and Angles (deg) of (η^5-C_5Me_5)(dppp)Ru=CCH(Ph)CH(CN)C$(CH_3)_2$O (7)

Ru−P1	2.341(2)	Ru−P2	2.331(2)
Ru−C1	1.943(8)	C1−C2	1.55(1)
C2−C3	1.55(1)	O1−C4	1.49(1)
C3−C4	1.54(1)	O1−C1	1.33(1)
C4−C5	1.50(1)	C3−C13	1.45(1)
C4−C6	1.52(1)	N1−C13	1.14(1)
P1−Ru−P2	89.96(8)	P1−Ru−C1	87.3(3)
P2−Ru−C1	89.9(2)	Ru−C1−O1	125.2(6)
Ru−C1−C2	128.2(6)	O1−C1−C2	106.2(7)
C2−C3−C4	105.0(7)	C1−C2−C3	103.3(6)
C3−C2−C7	116.3(7)	C4−C3−C13	112.5(7)
C1−C2−C7	114.1(7)	C1−O1−C4	117.1(6)
C3−C4−O1	100.7(6)	C2−C3−C13	115.3(8)
C3−C2−C7	116.3(7)	C4−C3−C13	112.5(7)
C3−C4−C5	117.0(8)	C3−C4−C6	112.9(8)
O1−C4−C5	107.7(7)	O1−C4−C6	105.6(7)
C5−C4−C6	111.6(7)		

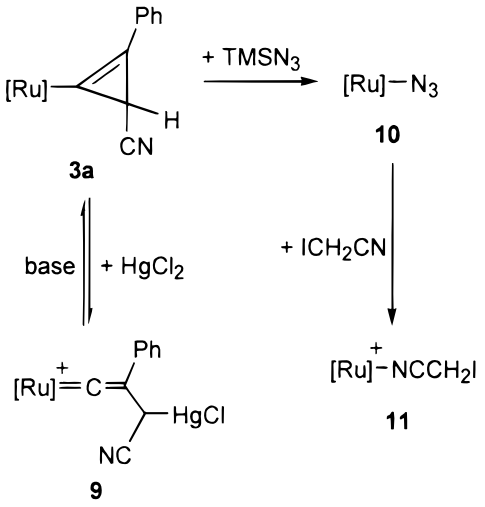
Reactions of Ruthenium Cyclopropenyl Complex 3a. Reactions of CF_3COOH with **3a** and **3b** readily gave **2a** and **2b**, respectively, indicating the basic character of the methine carbon of the three-membered ring. This protonation is different from the acid-induced demethoxylation of the iron cyclopropenyl complex $Cp(CO)_2Fe[C_3(OMe)(Ph)_2]$, containing a methoxy group on the three-membered ring.[31]

Treatment of **3a** with $HgCl_2$ produced the vinylidene complex [[Ru]=C=C(Ph)CH(CN)(HgCl)][Cl] (**9**) in 86% yield. As expected, the ^{31}P NMR spectrum of **9** displays two doublets at δ 37.88 and 32.82 with J_{P-P} = 50.39 Hz. Formation of **9** occurs by selective cleavage of the cyclopropenyl single bond near the metal center. Attempts to carry out cyclopropenation of **9** by using *n*-Bu_4NOH, *n*-Bu_4NF, and DBU resulted in cleavage of the C−Hg bond, yielding **3a** (Scheme 3).

The addition of 5 equiv of Me_3SiN_3 ($TMSN_3$) to **3a** in THF at room temperature initiated a color change from the light yellow solution of **3** to red initially, then

(39) Bruce, M. I.; Swincer, A. G.; Thomson, B. J.; Wallis, R. C. *Aust. J. Chem.* **1980**, *33*, 2605. (b) Garner, J.-A. M.; Irving, A.; Moss, J. R. *Organometallics* **1990**, *9*, 2836. (c) Adams, H.; Bailey, N. A.; Grayson, M.; Ridgway, C.; Smith, A. J.; Taylor, P.; Winter, M. J.; Housecroft, C. E. *Organometallics* **1990**, *9*, 2621.

Scheme 3



becoming a light orange after ca. 30 min, and, after 1 h, turning yellow again. The final product was recovered as $[Ru]N_3$ (**10**) (Scheme 3) in 78% yield. Recently[40] 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 $\{[Ru]NC-CH_2I\}[I_3]$ (**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 single bond, respectively. The N1−C2−C3 angle of 176.1(9)° is close to linear, indicating a C(sp) hybridization. The C2−C3−I1 angle of 109.8(5)° is typical for that of an idealized $C(sp^3)$ hybridization.

(40) Chang, K. H.; Lin, Y. C. *Chem. Commun.* **1998**, 1441.

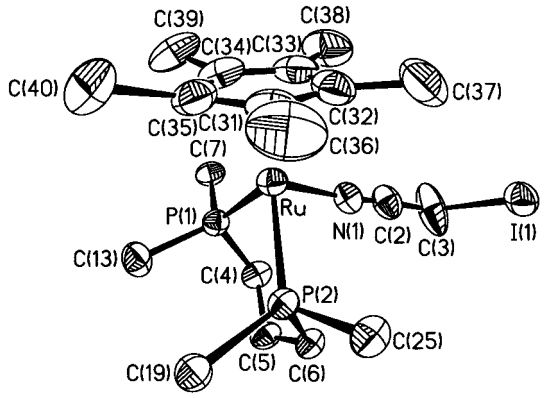


Figure 5. ORTEP drawing of **11** with thermal ellipsoids shown at the 30% probability level. For phenyl groups on dppp, only the ipso carbons are shown.

Table 5. Selected Bond Distances (Å) and Angles (deg) of $[(\eta^5\text{-}C_5Me_5)(dppp)RuNCCH_2I][I_3]$ (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)

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 −CN and $-CO_2CH_3$ in acetone. Treatment of cationic vinylidene complexes containing relatively weaker electron-withdrawing substituents such as C_6F_5, Ph, *p*-C_6H_4CN, and *p*-$C_6H_4CF_3$ 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 dihydrofuranyl 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 due to the electronic and steric effects. Treatment of **3** with $(CH_3)_3SiN_3$ 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 [Ru]C≡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 [[Ru]═C═C(Ph)CH$_2$CN][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: ^{1}H NMR (CDCl3) δ 7.47−6.82 (m, 25H, Ph), 3.22 (s, 2H, CH_2), 2.65 (m, 2PCH$_2$), 1.93 (m, PCH$_2$C*H*$_2$), 1.58 (s, 15H, 5CH$_3$); ^{31}P NMR ($CDCl_3$) δ 34.35; ^{13}C NMR ($CDCl_3$) δ 341.8 (t, C$_\alpha$, J_{C-P} = 17.9 Hz), 133.3−127.8 (Ph), 119.4 (C$_\beta$), 118.6 (CN), 104.7 (Cp), 29.4 (t, PCH$_2$, J_{C-P} = 17.9 Hz), 21.3 (PCH$_2$*C*H$_2$), 17.4 (CH_2CN), 10.3 (5CH$_3$); MS (*m*/*z*, Ru^{102}) 790.2 (M$^+$ − I), 750.2 (M$^+$ − I − CH_2CN), 649.1 (M$^+$ − I − CH_2CN − CCPh). Anal. Calcd for $C_{47}H_{48}NP_2RuI$: C, 61.57; H, 5.28; N, 1.53, Found: C, 62.37; H, 5.45; N, 1.44.

Complexes [[Ru]═C═C(Ph)CH$_2$R][Br] (R = CO_2CH_3, **2b** (85% yield); R = C_6F_5, **2c** (82% yield); R = Ph, **2d** (79% yield); R = *p*-C_6H_4CN, **2e** (83% yield); R = *p*-$C_6H_4CF_3$, **2f** (87% yield)) were prepared from the reaction of **1** with $BrCH_2CO_2CH_3$, $BrCH_2C_6F_5$, $BrCH_2C_6H_5$, $BrCH_2$(*p*-C_6H_4CN), and BrCH2(*p*-$C_6H_4CF_3$), respectively, using a procedure similar to that of **2a**. Spectroscopic data for **2b** are as follows: ^{1}H NMR ($CDCl_3$) δ 7.62−6.84 (m, 25H, Ph), 3.56 (s, 3H, OCH_3), 3.27 (s, 2H, CH_2), 2.71 (m, 2PCH$_2$), 2.02 (m, PCH$_2$C*H*$_2$), 1.56 (s, 15H, 5CH$_3$); ^{31}P NMR ($CDCl_3$) δ 35.10; ^{13}C NMR ($CDCl_3$) δ 345.1 (t, C$_\alpha$, J_{C-P} = 14.0 Hz), 171.5 (CO_2), 133.3−121.5 (Ph and C$_\beta$), 104.1 (Cp), 52.0 (OCH_3), 33.3 (CH_2), 29.1 (t, PCH$_2$, J_{C-P} = 18.4 Hz), 21.7 (PCH$_2$*C*H$_2$), 10.4 (5CH$_3$); MS (*m*/*z*, Ru^{102}) 823.3 (M$^+$ − Br), 750.2 (M$^+$ − Br − $CH_2CO_2CH_3$), 649.1 (M$^+$ − Br − $CH_2CO_2CH_3$ − CCPh). Anal. Calcd for $C_{48}H_{51}O_2P_2BrRu$: C, 63.85; H, 5.69. Found: C, 64.22; H, 5.83. Spectroscopic data for **2c** are as follows: ^{1}H NMR ($CDCl_3$) δ 7.44−6.76 (m, 25H, Ph), 3.97 (s, 2H, CH_2), 2.80 (m, 2PCH$_2$), 2.65 (m, PCH$_2$C*H*$_2$), 1.59 (s, 15H, 5CH$_3$); ^{31}P NMR ($CDCl_3$) δ 35.86; ^{13}C NMR ($CDCl_3$) δ 341.8 (t, C$_\alpha$, J_{C-P} = 14.5 Hz), 134.1−123.7 (Ph), 119.4 (C$_\beta$), 104.2 (Cp), 29.1 (t, PCH$_2$, J_{C-P} = 18.8 Hz), 21.8 (PCH$_2$*C*H$_2$), 20.1 ($CH_2C_6F_5$), 10.5 (5CH$_3$); MS (*m*/*z*, Ru^{102}) 931 (M$^+$ − Br), 750.2 (M$^+$ − Br − $CH_2C_6F_5$), 649.1 (M$^+$ − Br − $CH_2C_6F_5$ − CCPh). Anal. Calcd for $C_{52}H_{48}F_5P_2BrRu$: C, 61.78; H, 4.79. Found: C, 62.35; H, 4.93. Spectroscopic data for **2d** are as follows: ^{1}H NMR ($CDCl_3$) δ 7.90−6.86 (m, 25H, Ph), 3.82 (s, 2H, CH_2), 2.70 (m, 2PCH$_2$), 2.17 (m, PCH$_2$C*H*$_2$), 1.63 (s, 15H, 5CH$_3$); ^{31}P NMR ($CDCl_3$) δ 35.77; ^{13}C NMR ($CDCl_3$) δ 345.4 (t, C$_\alpha$, J_{C-P} = 10.1 Hz), 137.7−125.7 (Ph and C$_\beta$), 103.7 (Cp), 32.7 ($CH_2C_6H_5$), 29.2 (t, PCH$_2$, J_{C-P} = 19.2 Hz), 21.9 (PCH$_2$*C*H$_2$), 10.7 (5CH$_3$); MS (*m*/*z*, Ru^{102}) 841.4 (M$^+$ − Br), 750.2 (M$^+$ − Br − $CH_2C_6H_5$), 649.1 (M$^+$ − Br − $CH_2C_6H_5$ − CCPh). Anal. Calcd for $C_{52}H_{53}P_2RuBr$: C, 67.82; H, 5.80. Found: C, 68.25; H, 5.93. Spectroscopic data for **2e** are as follows: ^{1}H NMR ($CDCl_3$) δ 7.62−6.79 (m, 25H, Ph), 3.94 (s, 2H, CH_2), 2.77 (m, 2PCH$_2$), 2.13 (m, PCH$_2$C*H*$_2$), 1.59 (s, 15H, 5CH$_3$); ^{31}P NMR ($CDCl_3$) δ 35.46; ^{13}C NMR ($CDCl_3$) δ 344.6 (t, C$_\alpha$, J_{C-P} = 14.1 Hz), 134.1−124.8 (Ph), 119.2 (C$_\beta$), 118.7 (CN), 103.8 (Cp), 29.2 (t, PCH$_2$, J_{C-P} = 18.9 Hz), 21.8 (PCH$_2$*C*H$_2$), 32.6 ($CH_2C_6H_4CN$), 10.6 (5CH$_3$); MS (*m*/*z*, Ru^{102}) 946.2 (M$^+$ − Br), 750.2 (M$^+$ − Br − $CH_2C_6H_4CN$), 649.1 (M$^+$ − Br − $CH_2C_6H_4CN$ − CCPh). Anal. Calcd for $C_{53}H_{52}NP_2RuBr$: 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: ^{1}H NMR ($CDCl_3$) δ 7.59−6.83 (m, 25H, Ph), 3.89 (s, 2H, CH_2), 2.77 (m, 2PCH$_2$), 2.05 (m, PCH$_2$C*H*$_2$), 1.61 (s, 15H, 5CH$_3$); ^{31}P NMR ($CDCl_3$) δ 35.61; ^{13}C NMR ($CDCl_3$) δ 345.0 (t, C$_\alpha$, J_{C-P} = 16.3 Hz), 142.5−125.1 (Ph and C$_\beta$), 103.8 (Cp), 32.4 ($CH_2C_6H_4CN$), 29.2 (t, PCH$_2$, J_{C-P} = 19.5 Hz), 21.9 (PCH$_2$*C*H$_2$), 10.6 (5CH$_3$); MS (*m*/*z*, Ru^{102}) 989.2 (M$^+$ − Br), 750.2 (M$^+$ − Br − $CH_2C_6H_4CF_3$), 649.1 (M$^+$ − Br − $CH_2C_6H_4CF_3$ − CCPh). Anal. Calcd for $C_{53}H_{52}F_3P_2RuBr$: C, 64.37; H, 5.30. Found: C, 64.58; H, 5.49.

Synthesis of [Ru]C═C(Ph)CHCN (3a). To a 15 mL acetonitrile solution of complex **2a** (1.70 g, 1.854 mmol) was added an aliquot of *n*Bu$_4$NOH (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 × 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: ^{1}H NMR ($CDCl_3$) δ 7.72−7.03 (m, 25H, Ph), 2.65 (m, 2PCH$_2$), 1.93 (m, PCH$_2$C*H*$_2$), 1.35 (s, 15H, 5CH$_3$), 1.07 (s, 1H, CH); ^{31}P NMR ($CDCl_3$) δ 48.13, 45.52 (AB, J_{P-P} = 49.76 Hz); ^{13}C NMR ($CDCl_3$) δ 135.2−122.7 (Ph, and C$_\beta$), 134.0 (t, C$_\alpha$, J_{C-P} = 5.74 Hz), 114.0 (CN), 94.0 (Cp), 29.9 (t, PCH$_2$, J_{C-P} = 28.1 Hz), 24.1 (PCH$_2$*C*H$_2$), 13.7 (CH), 10.0 (5CH$_3$); MS (*m*/*z*, Ru^{102}) 790.1 (M$^+$ + 1), 751.2 (M$^+$−CHCN), 649.1 (M$^+$−CHCN−CCPh). Anal. Calcd for $C_{47}H_{47}NP_2Ru$: C, 71.55; H, 6.01; N, 1.78. Found: C, 72.31; H, 6.37; N, 1.55.

Synthesis of [Ru]C═C(Ph)CH(CO$_2$CH$_3$) (3b). To a 10 mL acetone solution of complex **2b** (500 mg, 0.554 mmol) was added an aliquot of (*n*Bu)$_4$NOH (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 × 5 mL of acetone, then dried under vacuum to give the product **3b** (340 mg, 77% yield). Spectroscopic data for **3b** are as follows: ^{1}H NMR ($CDCl_3$) δ 7.63−6.89 (m, 25H, Ph), 3.43 (s, 3H, OCH_3), 2.43 (m, 4H, PCH$_2$), 2.02 (m, PCH$_2$C*H*$_2$), 1.60 (s, 1H, CH), 1.34 (s, 15H, 5CH$_3$); ^{31}P NMR ($CDCl_3$) δ 47.73, 43.00 (AB, J_{P-P} = 50.18 Hz); ^{13}C NMR ($CDCl_3$) δ 183.6 (CO_2), 134.0−119.4 (Ph and Cα), 104.2 (C$_\beta$), 89.1 (Cp), 52.1 (O*C*H$_3$), 26.8 (t, J_{C-P} = 13.7 Hz, PCH$_2$), 21.5 (PCH$_2$*C*H$_2$), 10.0 (CH), 10.5 (5CH$_3$), 9.7 (CH); MS (*m*/*z*, Ru^{102}) 823.1 (M$^+$ + 1), 750.2 (M$^+$ − CHCO$_2$CH$_3$), 649.1 (M$^+$ − CHCO$_2$CH$_3$ − CCPh). Anal. Calcd for $C_{48}H_{50}O_2P_2Ru$: C, 70.14; H, 6.13. Found: C, 71.23; H, 6.37.

Synthesis of [Ru]C═C(Ph)CH(CN)C(CH$_3$)$_2$O (4). To a 15 mL acetone solution of **2a** (500 mg, 0.634 mmol) was added an aliquot of *n*Bu$_4$NOH (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 × 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: ^{1}H NMR ($CDCl_3$) δ 7.58−6.17 (m, 25H, Ph), 2.86 (t, PCH$_2$, J_{H-P} = 9.85 Hz), 2.54 (m, PCH$_2$C*H*$_2$), 2.86 (t, PCH$_2$, J_{H-P} = 13.57 Hz), 1.57 (s, 1H, CH), 1.22 (s, 6H, 2CH$_3$), 1.08 (s, 15H, 5CH$_3$); ^{31}P NMR ($CDCl_3$) δ 45.43, 39.11 (AB, J_{P-P} = 52.21 Hz); ^{13}C NMR ($CDCl_3$) δ 145.2 (O*C*(CH$_3$)$_2$), 135.1−123.6 (Ph, C$_\alpha$ and C$_\beta$), 113.1 (CN), 93.3 (Cp), 31.9 (t, PCH$_2$, J_{C-P} = 18.7 Hz), 22.1 (P*C*H$_2$), 9.6 (CH), 10.4 (5CH$_3$); MS (*m*/*z*, Ru^{102}) 848.3 (M$^+$ + 1), 790.2 (M$^+$ − CH$_3$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)$_2$O]-[I] (5a). A Schlenk flask was charged with ICH2CN (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 (O*C*(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, *C*HCN), 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 C52H55N2OP2RuI: 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)$_2$O]-[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 (O*C*(CH_3)$_2$), 70.3 (*C*H_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 (*C*HCN), 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)$_2$O][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 (O*C*(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)$_2$O][CF_3-COO] (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, C*H*Ph), 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 (O*C*(CH_3)$_2$), 70.2 (*C*HPh), 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 (*C*HCN), 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)$_2$O]-[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 (O*C*(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 $(C_5Me_5)(dppp)RuC{=}C(Ph)CHCN$ (3a), $(C_5Me_5)(dppp)RuC{=}C(Ph)CH(CN)C(CH_3)_2O$ (4), $[(C_5Me_5)(dppp)Ru{=}C{-}C(Ph){=}C(CN)C(CH_3)_2O][I]\cdot 2CHCl_3$ (6), $[(C_5Me_5)(dppp)Ru{=}CCH(Ph)CH(CN)C(CH_3)_2O][CF_3COO]\cdot 1/2CF_3COOH$ (7), and $[(C_5Me_5)(dppp)RuNCCH_2I][I_3]$ (11)

	$C_{47}H_{47}NP_2Ru$, **3a**	$C_{50}H_{53}NOPRu$, **4**	$C_{52}H_{53}Cl_6INOP_2Ru$, **6**	$C_{54}H_{55.5}Cl_3F_{4.5}NO_4P_2Ru$, **7**	$C_{39}H_{43}I_4NP_2Ru$, **11**
space group	$P2_1/n$	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
cryst syst	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic
a, Å	16.1153(3)	11.2771(3)	21.4873(4)	12.1587(5)	15.5340(1)
b, Å	12.2925(1)	17.8994(4)	13.2421(3)	19.1984(8)	13.2322(1)
c, 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
V, Å^3	3946.28(11)	4816.1(2)	5360.5(2)	5237(6)	4253.98(6)
Z	4	4	4	4	4
cryst dimens, 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 *R* indices [$I > 2\sigma(I)$]	R1 = 0.0279, wR2 = 0.0715	R1 = 0.0702, wR2 = 0.1702	R1 = 0.0542, wR2 = 0.1282	R1 = 0.0964, wR2 = 0.1848	R1 = 0.0491, wR2 = 0.1162
R indices (all data)	R1 = 0.0394, wR2 = 0.0779	R1 = 0.1166 wR2 = 0.1928	R1 = 0.0945, wR2 = 0.1456	R1 = 0.1487, wR2 = 0.2080	R1 = 0.0593, wR2 = 0.1245

N_3). Anal. Calcd for $C_{37}H_{41}N_3P_2Ru$: C, 64.33; H, 5.98; N, 6.08. Found: C, 64.46; H, 6.10; N, 5.93.

Synthesis of [[Ru]NCCH$_2$I][I$_3$] (11). A Schlenk flask was charged with ICH_2CN (100 μL, 1.45 mmol) and **10** (100 mg, 0.145 mmol) in 10 mL of CH_2Cl_2. 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: ^{1}H NMR ($CDCl_3$) *δ* 8.07−6.83 (m, 25H, Ph), 4.50 (s, 2H, CH_2), 2.59 (m, 2H, PCH_2), 2.43 (m, 2H, PCH_2CH_2), 2.00 (m, 2H, PCH_2), 1.54 (s, 15H, $5CH_3$); ^{31}P NMR ($CDCl_3$) *δ* 35.01; ^{13}C NMR ($CDCl_3$) *δ* 133.8−124.7 (Ph, C_α and C_β), 119.4 (CN), 93.2 (Cp), 50.9 (CH_2), 29.4 (t, J_{C-P} = 8.22 Hz, PCH_2), 20.3 (PCH_2CH_2), 9.7 ($5CH_3$); MS (*m*/*z*, Ru^{102}) 816.2 ($M^+ + 1 - I_3$), 776.1 ($M^+ - I_3 - CH_2CN$), 649.3 ($M^+ - I_4 - CH_2CN$). Anal. Calcd for $C_{39}H_{42}NP_2RuI_4$: 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 mm^3 was glued to a glass fiber and mounted on a SMART CCD diffractometer. The data were collected using 3 kW sealed-tube molybdenum Kα radiation (T = 295 K). Exposure time was 5 s per frame.[42] SADABS[43] (Siemens area detector absorption) absorption correction was applied, and decay was negligible. Data were processed and the structures were solved and refined by the SHELXTL[44] program. The structure was solved using direct methods and confirmed by Patterson methods refining on intensities of all data (20 610 reflections) to give wR1 = 0.0579 and wR2 = 0.1221[45] for 20 610 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 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

(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.

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

(45) GOF = $[\sum[w(F^2_o - F^2_c)^2]/(n-p)]^{1/2}$, where *n* and *p* denote the number of data and parameters. R1 = $(\sum||F_o| - |F_c||)/\sum|F_o|$, wR2 = $[\sum[w(F^2_o - F^2_c)^2]/\sum[w(F^2_o)^2]]^{1/2}$ where $w = 1/[\sigma^2(F^2_o) + (aP)^2 + bP]$ and $P = [(\max; 0, F^2_o) + 2F^2_c]/3$.