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Published on Web 12/01/2005

Intramolecular Metathesis of a Vinyl Group with Vinylidene C=C Double Bond in Ru Complexes

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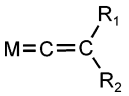
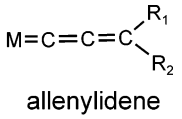
Abstract: The cationic complex {[Ru]=C=CHCPh$_2$CH$_2$CH=CH$_2$}BF$_4$ (**3a**, [Ru] = (η^5-C$_5$H$_5$)(PPh$_3$)$_2$Ru) in solution transforms to {[Ru]=C=CHCH$_2$CPh$_2$CH=CH$_2$}BF$_4$ (**4a**) via a new metathesis process of the terminal vinyl group with the C=C of the vinylidene group which is confirmed by ^{13}C labeling studies. This transformation is irreversible as revealed by deuteration and decomplexation studies. The cationic complex {[Ru]=C=CHCPh$_2$CH$_2$CMe=CH$_2$}BF$_4$ (**3b**) undergoes a cyclization process yielding **6b** containing a η^2-cyclic allene ligand which is fully characterized by single-crystal X-ray diffraction analysis. Analogous complexes **4a′** and **6b′** ([Ru] = (η^5-C$_5$H$_5$)(dppe)Ru) containing dppe ligands were similarly obtained from protonation of the corresponding acetylide complexes via formation of vinylidene intermediate. Protonation of the acetylide complex containing a terminal alkynyl group [Ru]-C≡CCPh$_2$CH$_2$C≡CH (**2c**) generates the vinylidene complex {[Ru]=C=CHCPh$_2$CH$_2$C≡CH}BF$_4$ (**3c**) which again undergoes an irreversible transformation to give {[Ru]=C=CHCH$_2$CPh$_2$C≡CH}BF$_4$ (**4c**) possibly via a π-coordinated alkynyl complex followed by hydrogen and metal migration. No similar transformation is observed for the analogous dppe complex **3c′**. With an extra methylene group, complex {[Ru]=C=CHCPh$_2$CH$_2$CH$_2$CH=CH$_2$}BF$_4$ (**3d**) and complex {[Ru]=C=CHCPh$_2$CH$_2$Ph}BF$_4$ (**3e**) are stable. The presence of a gem-diphenylmethylene moiety at the vinylidene ligand with the appropriate terminal vinyl or alkynyl group along with the correct steric environment implements such a novel reactivity in the ruthenium vinylidene complexes.

Introduction

Free vinylidene is a high-energy tautomer of alkyne and could be effectively stabilized by coordination to transition metals.[1] Novel chemical properties of the resulting metal vinylidene complexes are valuable for organic transformations. For instance, vinylidene complexes of various metals commonly function as strategic intermediates for catalytic conversion of alkynes such as cycloaromatization of conjugated enediynes,[2] dimerization of terminal alkynes,[3] and addition of oxygen, nitrogen, and carbon nucleophiles to alkynes.[4] Furthermore, some vinylidene complexes have been exploited as catalyst precursors for olefin-metathesis reactions.[5] Reactivities of metal vinylidene complexes are rationalized by taking electrophilicity of vinylidene α-carbon, nucleophilicity of vinylidene β-carbon, and highly unsaturated structures of the vinylidene ligands into consideration.[1a] With one more carbon atom, a metal allenylidene complex[6] is also of interest for the building of innovative carbon-rich architectures[7] and material science.[8]



vinylidene



allenylidene

Owing to the invention of a common method of approach by easy activation of propargylic alcohols,[9] the chemistry of metal allenylidenes has been quickly elaborated. Nowadays nucleophilic addition to the allenylidene ligand is considered

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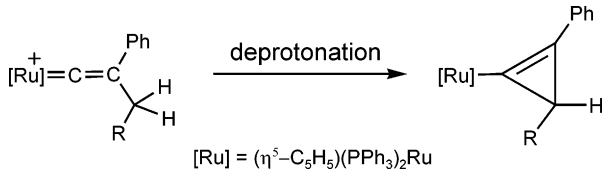
as an alternative synthesis of a metal vinylidene complex making various kinds of vinylidene complexes available for exploitation. We previously reported[10] synthesis of ruthenium cyclopropenyl complexes by deprotonation reaction of the readily accessible metal vinylidene complex containing a $-CH_2R$ group bound to C_β of the vinylidene ligand.



Our attempts to prepare a four-membered ring ligand have prompted us to synthesize vinylidene complexes containing a $-CPh_2CH_2R$ group bound to C_β of the vinylidene ligand. A number of such complexes are successfully prepared via alkylation of metal allenylidene by using Grignard reagents.[11] Surprisingly, with the presence of a terminal vinyl group, the metal vinylidene complex $[Ru]=C=CHCPh_2CH_2CH=CH_2^+$ displays novel intramolecular metathesis reactivity between the two C=C double bonds. Unlike electrophilic and nucleophilic additions to the vinylidene ligand, the cycloaddition of the C=C double bond of a vinylidene ligand is much less studied. It is well-known that the [2 + 2] cycloaddition of alkenes and/or alkynes represents an important approach for the synthesis of cyclobutane derivatives.[12] A thermally forbidden process by the Woodward−Hoffmann rules,[13] this cycloaddition has been achieved photochemically,[14] by thermal reactions via biradical intermediates,[15] by the use of Lewis acid catalysts,[16] and by the use of transition metal catalysts.[17] To date, the range of substrates which undergo [2 + 2] reactions with transition metals is rather restricted. Reactions of strained alkenes have received the most attention, and further studies to expand the scope of this reaction are needed.[26,27] Herein we report a novel transformation of the vinylidene ligand involving metathesis of the C=C double bond of the vinylidene ligand and a terminal vinyl group tethered on the ligand.

Results and Discussion

Preparation of Ruthenium Allenylidene Complexes. The reported preparation of a ruthenium diphenylallenylidene complex in the literature[28] is modified to obtain $[Ru]=C=C=CPh_2^+$, (**1**, [Ru] = $Cp(PPh_3)_2Ru$) in high yield. Many other ruthenium diphenylallenylidene complexes are known in the literatures.[9,29] The reaction of **1** with Grignard reagents $R-CH_2MgBr$ yield the acetylide complexes $[Ru]-C\equiv C-C(Ph)_2CH_2R$ (**2a**, R = $CH=CH_2$; **2b**, R = $CMe=CH_2$; **2c**, R = C≡CH; **2d**, R = CH_2-$CH=CH_2$; **2e**, R = Ph; Scheme 1) all in high yield. Characteristic spectroscopic data of **2a**, **2b**, **2c**, **2d**, and **2e** are comparable with that of analogous indenyl complexes in the literature.[11a] Complexes **2a**−**2e** are characterized by IR, ^{31}P, ^1H, and ^{13}C NMR spectroscopy. The IR spectra of these acetylide complexes show typical ν(C≡C) absorption bands within 2077−2084 cm^{-1}. In the ^{13}C NMR spectra ^{13}C resonances of the acetylide ligand fall in the ranges of δ 97.1−98.6 for C_α and 114.4−115.2 for C_β. In the ^1H NMR spectrum of **2a**, the doublet resonance at δ 3.27 with J_{H-H} = 6.0 Hz is assigned to the internal methylene group. Corresponding methylene resonances for complexes **2b**, **2c**, **2d**, and **2e** appear at δ 3.29, 3.31, 2.58, and 3.79, respectively.

Novel Metathesis Reactions. Protonation of complexes **2a**−**2e** by HBF_4 in diethyl ether at 0 °C gave the corresponding vinylidene complexes $[Ru]=C=CHC(Ph)_2CH_2R^+$ (**3a**, R = $CH=CH_2$; **3b**, R = $CMe=CH_2$; **3c**, R = C≡CH; **3d**, R = CH_2-$CH=CH_2$; **3e**, R = Ph) as a solid precipitate all with over 90%

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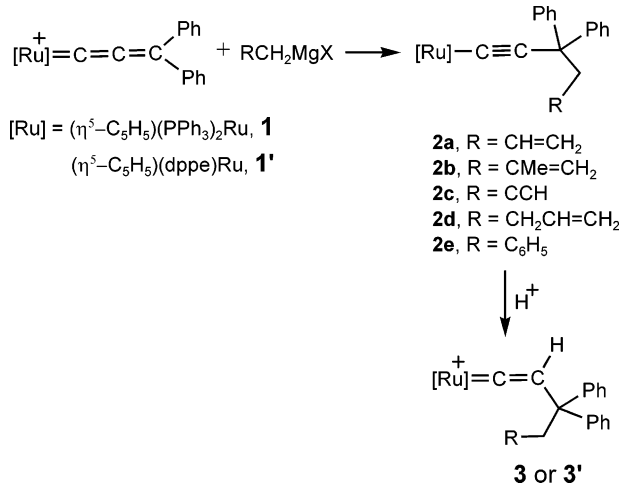
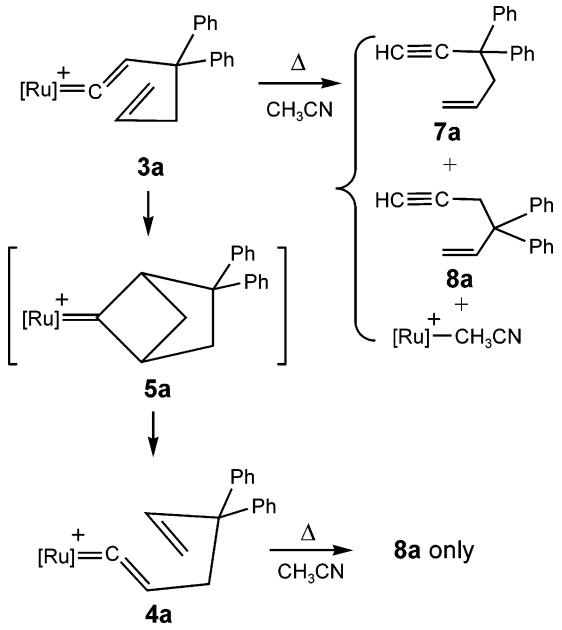
Scheme 1



Scheme 2



yield. Complexes **3d** and **3e** are stable vinylidene compounds even at 75 °C. Interestingly, vinylidene complexes **3a**, **3b**, and **3c** all display interesting reactivity possibly due to the presence of the gem-diphenyl group and the unsaturated functional group at a proper location of the vinylidene ligand.

Treatment of complex **2a** with HBF_4 affords the cationic complex $[Ru]{=}C{=}CHC(Ph)_2CH_2CH{=}CH_2^+$ (**3a**) as a light pink powder. When complex **3a** is dissolved in $CDCl_3$ or CH_2Cl_2 at room temperature, a novel transformation takes place and $[Ru]{=}C{=}CHCH_2CPh_2CH{=}CH_2^+$ (**4a**) is isolated in 90% yield in ca. 12 h (see Scheme 2). With a chelating diphenylphosphinoethane (dppe) ligand replacing the two PPh_3 ligands, complex $[Ru']{=}C{=}CHC(Ph)_2CH_2CH{=}CH_2^+$ ($[Ru'] = (\eta^5\text{-}C_5H_5)$(dppe)Ru, **3a′**) undergoes the same metathesis transformation giving **4a′** with a much faster rate of reaction.

If the CH_3CN solution of complex **3a** is heated to reflux, three products, cationic metal acetonitrile $[Ru]NCCH_3^+$, 4,4-diphenyl-hex-1,5-enyne (**7a**), and 3,3-diphenyl-hex-1,5-enyne (**8a**), in a 3:2:1 ratio are isolated in high yield. Complex **4a** can be observed at the initial stage of the reaction at room temperature, and eventually **7a**, **8a**, and $[Ru]NCCH_3^+$ are isolated. Thermolysis of **4a** in CH_3CN yields only **8a** quantitatively indicating that the transformation of **3a** to **4a** is irreversible (see Scheme 2). Formation of alkyne from metal vinylidene in acetonitrile has been reported in thermolysis of the analogous indenyl vinylidene complex. However the reaction of the indenyl compound yielded only 1,5-enyne **7a**.

Characterization of **3a** and **4a** is achieved by a spectroscopic method as well as elemental analysis. Significant differences in the spectroscopic data of **3a** and **4a** leading to disclosure of the structural feature can be undoubtedly discerned. Mainly the coupling patterns of ^1H resonances of vinylidene and vinyl protons of the ^1H COSY NMR spectra reveal important structural information. In the ^1H NMR spectrum of **3a**, the broad triplet resonance of the vinylidene proton at δ 4.45 with $J_{H-P} = 3.0$ Hz shows coupling only with the phosphine ligands. For **4a**, the corresponding ^1H resonance of the vinylidene proton at δ 4.40, in addition to being coupled with two phosphine ligands, is found to be coupled with the methylene protons at δ 3.09 with $J_{H-H} = 7.8$ Hz indicating direct connectivity of the methylene group to C_β of the vinylidene ligand. For **3a**, the multiplet resonance at δ 5.02 assignable to the methyne proton of the vinyl group is coupled to the resonance at δ 3.06 with $J_{H-H} = 6.0$ Hz assignable to the saturated internal methylene group. But in **4a**, the corresponding vinyl proton at δ 3.09 only couples with the resonances of the terminal olefinic $=CH_2$ group indicating no neighboring CH_2 group thus signifying direct bonding of the vinyl ligand to the CPh_2 group. In addition, the relevant spectroscopic feature of **4a** is the characteristic C_α resonance as a triplet at δ 345.6 with $J_{P-C} = 15.1$ Hz in the ^{13}C NMR spectrum. All these spectroscopic data support the proposed formula for **4a**. Spectroscopic data of **7a** and **8a**, particularly the ^1H NMR spectra, are consistent with their formulas.

Such a transformation could be interpreted by a novel metathesis process between the terminal vinyl group and the C═C of the vinylidene ligand of **3a** first giving the possible cyclobutylidene intermediate **5a** shown in the Scheme 2. Namely, a regiospecific [2+2] cycloaddition of two double bonds leads to formation of the four-membered ring. This is followed by a retro-cycloaddition to give **4a**. A somewhat similar cycloaddition, namely, the first half of our metathesis reaction, has been reported by Gimeno's group for a ruthenium vinylidene complex containing an allylphosphine ligand.[30] However, in **3a**, a further step causes complete metathesis of two double bonds.

When a stoichiometric amount of CF_3COOD is used in treating **2a** leading to **4a** in $CDCl_3$, a mixture of deuterated products was observed (Scheme 3). The vinylidene proton and the methyne proton of the terminal vinyl group are partly deuterated. No deuterium incorporation takes place at the terminal CH_2 of the vinyl group or at the saturated methylene group. In the proton NMR spectrum, the intensity ratio of vinylidene proton to methyne proton is 3:2. If an excess amount of CF_3COOD is used in the protonation of **2a**, both hydrogen atoms are replaced by deuterium giving **4a-D**$_2$. However, addition of D^+ to **4a** results in formation of only **4a-D**$_a$, but no **4a-D**$_b$ is observed. The deuterium incorporation is observed to

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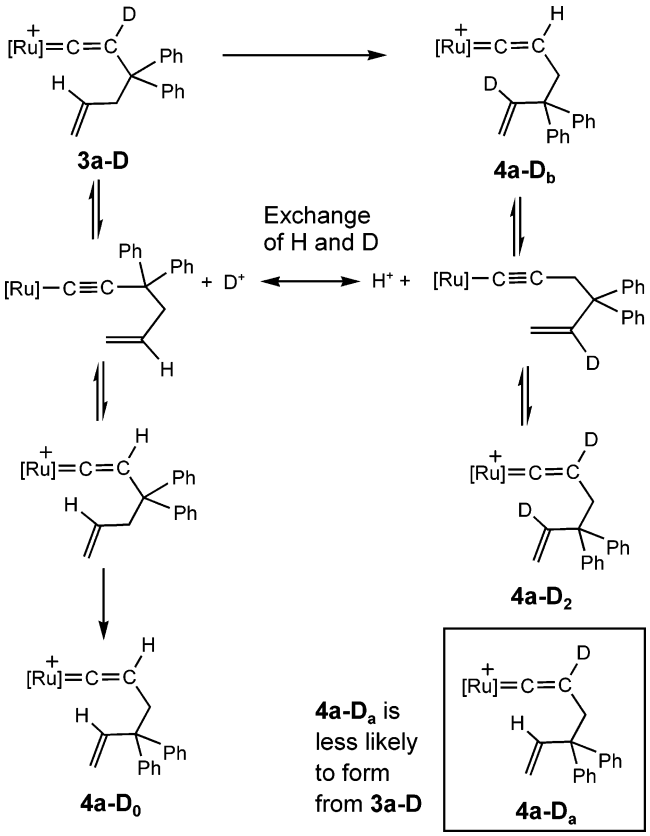
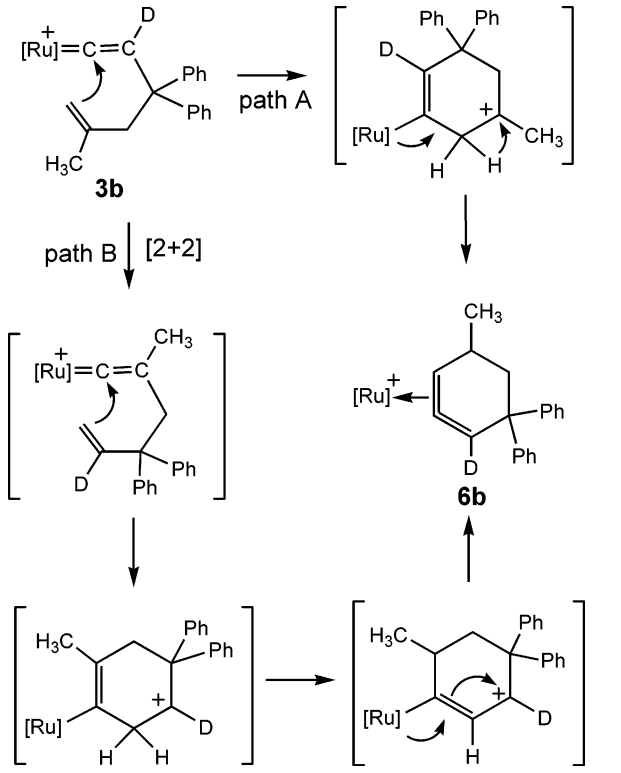
Scheme 3



take place only at the vinylidene hydrogen indicating that transformation of **3a** to **4a** is irreversible. The H−D exchange is proposed to proceed via the pathway shown in Scheme 3. Metathesis of **3a-D** before H−D exchange should result in formation of **4a-D**$_b$. Fast transformation of both vinylidene complexes to acetylide complexes and proton and/or deuterium should then create an opportunity for exchange of proton and deuterium leading to the formation of **4a-D**$_0$ and **4a-D**$_2$. It is less likely to obtain **4a-D**$_a$ from **3a-D** with only one deuteration at the vinylidene group. In the ^{1}H NMR spectrum of the product isolated from **3a-D**, we actually observed a vinylidene proton and internal vinyl proton of a mixture of **4a-D**$_0$, **4a-D**$_b$, and **4a-D**$_2$. For a much faster transformation of vinylidene to acetylide relative to that of metathesis, a statistical distribution of **4a** (no **4a-D**$_a$) should be obtained and the ratio of the vinylidene proton to the internal vinyl proton is 2:1. Considering the rate of metathesis is also fast, the observed ratio (3:2) is in reasonable agreement with the theoretical value.

Definite evidence for the metathesis is obtained from a ^{13}C labeling study of the reaction. The ^{13}C labeling at both C$_\alpha$ and C$_\beta$ for **1** is readily achieved by using TMS^{13}C≡^{13}CH to prepare the propargyl alcohol H^{13}C≡^{13}CC(Ph)$_2$OH for the synthesis of ^{13}C$_\alpha$,^{13}C$_\beta$-allenylidene complex **1** from which the isolated product **4a** via **2a** and **3a** sequentially is found to have ^{13}C labeling at C$_\alpha$ (triplet at δ 345.6 with J_{C-P} = 15.5 Hz) and an internal vinyl CH unit (singlet at δ 143.8) with no C−C coupling between the two carbon atoms. Portions of ^{13}C spectra of complexes **3a** (the second trace from the top) and **4a** (the middle trace) obtained from **2a** (the top trace) with 25% ^{13}C enrichment at C$_\alpha$ and C$_\beta$ are shown in Figure 1. The J_{C-C} of 60.2 Hz between two enriched carbon atoms is clearly seen in **3a**, indicating direct connectivity. Evidence of intramolecular metathesis leading to separation of two carbon atoms is noticeably observed by the disappearance of such a C−C coupling between resonances of two enriched carbon atoms for **4a**.

Scheme 4



The indenyl analogue of **3a** has been reported[11a] by Gimeno and co-workers; however, no such transformation has been observed. Instead, with the presence of a vinylphosphine bound to the ruthenium metal center, the [2+2] cycloaddition of the C=C bond of the vinylidene ligand and the vinyl group of the phosphine ligand readily occurred.[30a] It seems that intricate steric or electronic demand is required for an intramolecular metathesis to take place.

Formation of Cyclic Allene from 3b. The vinylidene complex **3b** undergoes a different transformation process to give the cyclic allene complex **6b** in high yield; see Scheme 4. The reaction takes place as soon as **3b** is dissolved in solution, and the reaction is completed in 10 min at room temperature. In the ^{31}P NMR spectrum of **6b** two resonances at δ 41.3 and 40.9 with an AB pattern are observed indicating the presence of a stereogenic carbon center in the six-membered ring ligand. The ^{1}H NMR spectrum of **6b** displays resonances attributed to one methyl, one diastereotopic methylene, and three methyne groups. Resonances of two allenic hydrogens appear at δ 5.39 and 2.70 with the latter showing J_{P-H} = 9.5 Hz thus assignable to the coordinated portion of the allene ligand. Resonances of two methyne and a methyl group are overlapped in the region of δ 1.55 and 1.66. The ^{1}H−COSY 2D NMR spectrum reveals couplings of all relevant resonances. In addition, the very pertinent spectroscopic feature of **6b** is the characteristic doublet of the doublet ^{13}C resonance at δ 144.7 with J_{P-C} = 22.6, 2.5 Hz assignable to the central carbon of the allene ligand in the ^{13}C NMR spectrum. Protonation of complex **2b′** containing a dppe ligand gave **6b′** directly in 97% yield. The vinylidene complex was not observed. Both **6b** and **6b′** in their solid state

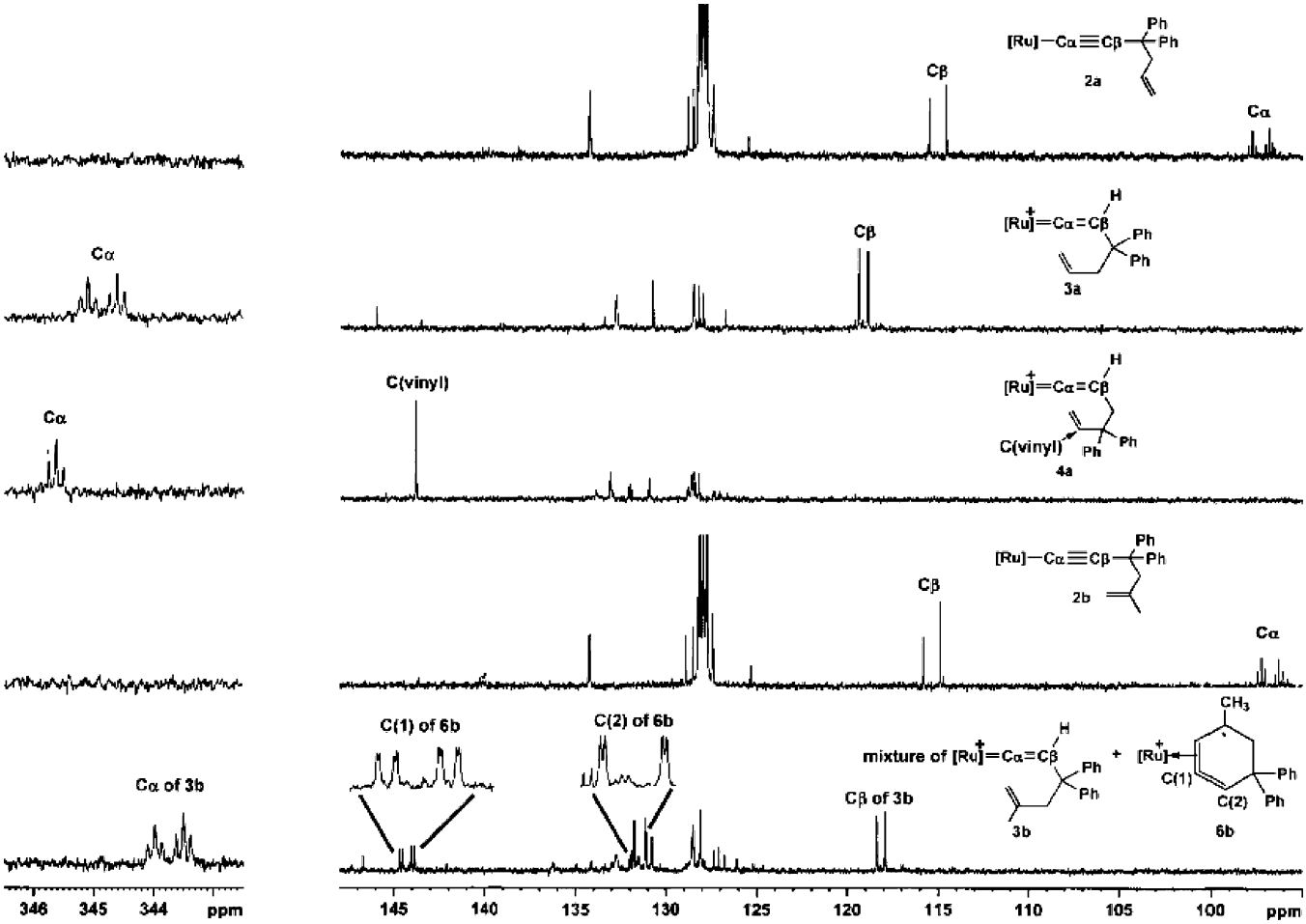


Figure 1. Part of ^{13}C NMR spectra of Ru complexes **2a**, **3a**, **4a**, **2b**, and a mixture of **3b** and **6b** prepared from 25% ^{13}C enriched $[Ru]=^{13}C=^{13}C=C(Ph)_2^+$ complex. For atom labeling, see inserted structure.

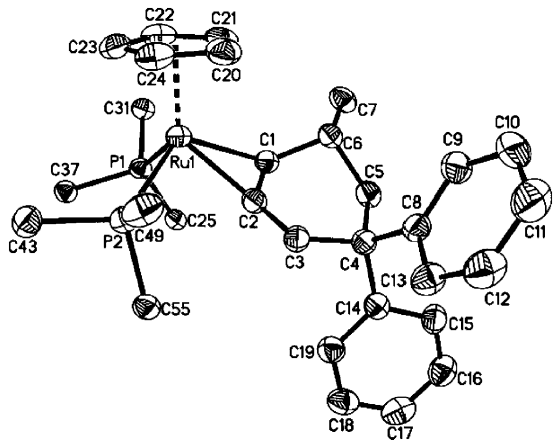


Figure 2. An ORTEP plot of complex **6b** drawn at the 30% probability level. Phenyl groups except the C(ipso) atoms on the phosphine ligand have been omitted for clarity.

Table 1. Selected Bond Lengths [Å] and Angles [deg] for Complex **6b**

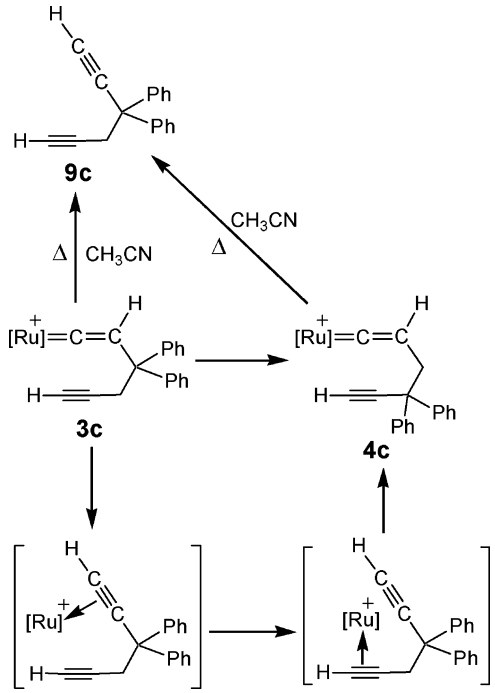
Ru(1)−P(1)	2.3724(11)	Ru(1)−P(2)	2.3930(12)
Ru(1)−C(1)	2.225(4)	Ru(1)−C(2)	2.088(4)
C(1)−C(2)	1.396(6)	C(2)−C(3)	1.326(6)
C(1)−C(6)	1.526(6)	C(3)−C(4)	1.518(6)
C(5)−C(6)	1.549(6)	C(4)−C(5)	1.558(6)
C(2)−C(1)−C(6)	111.8(4)	C(1)−C(2)−C(3)	126.9(4)
C(2)−C(3)−C(4)	119.8(4)	C(3)−C(4)−C(5)	110.2(4)
C(4)−C(5)−C(6)	115.8(4)	C(1)−C(6)−C(5)	101.4(3)

are stable, but **6b** decomposed in solution in 4 h at room temperature and **6b′** is stable.

Single crystals of **6b** suitable for X-ray diffraction analysis are obtained by recrystallization from acetone/diethyl ether. The solid-state structure is determined. An ORTEP drawing is shown in Figure 2, and representative bond lengths and angles are listed in Table 1. The coordination around the Ru atom can be described as a three-legged piano stool. The Ru−C(1) and Ru−C(2) bond lengths of 2.225(4) and 2.088(4) Å are in the range of a regular Ru−C bond for a ruthenium-allene coordination in other crystallographically characterized ruthenium allene complexes.[3a] The C(1)−C(2) bond length of 1.396(6) Å is in the range of that of a regularly coordinated double bond. The uncoordinated double bond of the allene ligand is slightly shorter (1.326(6) Å). The bond angles C(6)−C(1)−C(2) and C(1)−C(2)−C(3) of 111.8(4)° and 126.9(4)°, respectively, reveal the effect of metal coordination of one double bond.

Transformation of **3b** to **6b** could proceed via pathway **A** or **B** depicted in Scheme 4. With a methyl group at the vinyl group, complex **3b** undergoes a C−C bond formation between the terminal vinyl carbon atom and C_α giving a six-membered ring ligand with a stereogenic carbon center. This is followed by metal and proton migration to give the product (pathway **A**). However, the transformation could alternatively proceed via the same [2+2] cycloaddition pathway **B** as that in **3a** followed by the same C−C bond formation mentioned above with a 1,3

Scheme 5



hydrogen shift to yield **6b**. Deuteration should cause scrambling of deuterium for the reaction proceeding via the pathway **B** which is not experimentally observed. Considering the much faster rate of the reaction and the presence of a more stable tertiary carbocation, we believe this transformation could preferably proceed via pathway **A**.

A labeling study using $H^{13}C{\equiv}{}^{13}CC(Ph)_2OH$ for the preparation of **3b** reveals that the reaction proceeds via pathway **A** giving the product **6b** with labeling at two neighboring allenyl carbon atoms (δ 144.3, 131.4 with J_{C-C} = 81.4 Hz); see the bottom trace of Figure 1 which is the ^{13}C NMR spectrum of a mixture containing equal amounts of **3b** and **6b**. The ^{13}C NMR spectrum of **2b** with 25% enriched ^{13}C at C_α and C_β is also shown in Figure 1 for comparison.

Protonation of 2c. Vinylidene complex **3c** with a terminal alkynyl group on the chain bound at the vinylidene ligand is obtained in almost quantitative yield from the protonation reaction of **2c**. Complex **3c** is stable at room temperature. However, when heated to 56 °C, complex **3c** in solution is converted to **4c** in 4 h; see Scheme 5. If the thermolysis is carried out in CH_3CN, organic 1,5-diyne **9c** is obtained in high yield. Again ^1H NMR spectra of **3c** and **4c** are informative illuminating their structural features. The coupling pattern on the terminal alkynyl proton and vinylidene proton noticeably discloses the structural information. For **3c**, the resonance at δ 4.81 assignable to the vinylidene proton only couples with two phosphine ligands. But the corresponding resonance at δ 4.67 for **4c** is observed to have additional coupling to the methylene protons at δ 3.09 with J_{H-H} = 7.8 Hz indicating direct connectivity of the methylene group with the vinylidene ligand. Transformation of **3c** to **4c** could proceed via formation of a π-coordinated alkyne complex from **3c** followed by metal migration to the terminal alkynyl group (see Scheme 5). Therefore it is not surprising to observe formation of $\alpha\omega$-bisalkynyl compound **9c** when the reaction is carried out in CH_3CN. The driving force of such a transformation could be attributed to the steric effect between the gem-diphenyl group and the metal fraction. Surprisingly, the analogous complex **3c′** containing the dppe ligand would not undergo a similar transformation even under thermolytic conditions. This may indicate that, in addition to the steric effect, a proper orientation of two alkynyl groups is required such that the metal moiety could migrate between two C≡C triple bonds. A slight difference in steric or electronic environment deters such a transformation.

Treatment of **2d** with acid affords the vinylidene complex **3d** in almost quantitative yield. However even with a terminal vinyl group tethered on the vinylidene ligand for **3d**, no metathesis of the two double bonds is observed. Thermolysis in toluene causes extensive decomposition of **3d**. Both 5-methylenebicyclo[2,1,1]hexane and 6-methylenebicyclo[3,1,1]-heptane are known.[31] And a simple calculation seems to indicate that the latter has less ring strain. However, we do not see formation of a metathesis product. As expected, complex **3e** is also a stable compound. The fact that complex **3d** is stable with respect to the metathesis process could reflect that, even with the presence of a gem-diphenyl substituted group imposing the steric effect, proper conditions do not exist in this complex like the situation for the allyl terminus in **3a** and **3b**. The fact that the vinylidene complex **3d** failed to react may exemplify that the reactivity of a given vinylidene is highly sensitive to the structural changes at a site remote from the reacting double bond.

Concluding Remark

In summary, ruthenium complexes $\{[Ru]{=}C{=}CHCPh_2CH_2R\}BF_4$ **3a**−**3e** containing vinylidene ligands tethering with a terminal vinyl or alkynyl group were synthesized. For **3d** (R = $CH_2CH{=}CH_2$) and **3e** (R = Ph), normal behavior of a vinylidene complex was observed. However, a novel intramolecular metathesis process causes irreversible transformation of **3a** (R = $CH{=}CH_2$) to **4a**. Transformation of **3b** (R = $CMe{=}CH_2$) to the cyclic allene complex **6b** involved a C−C bond formation giving a six-membered ring and a change of coordination to a η^2-allene mode. For **3c** (R = C≡CH), a metal moiety could also irreversibly migrate to the terminal alkynyl group to give **4c** possibly with less steric demand between the metal center and the ligand. In vinylidene complexes **3a**, **3b**, and **3c**, a gem-diphenyl moiety along with an unsaturated functional group properly aligned with the vinylidene ligand in a particular orientation could be the reason for such a novel reactivity to take place. In contrast, the vinylidene complexes **3d** and **3e** failed to react, illustrating that the reactivity of a given vinylidene is highly sensitive to the structural changes at a site remote from the reacting double bond.

Experimental Section

General Procedures. The manipulations were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. All reagents were obtained from commercial suppliers ($TMS^{13}C{\equiv}{}^{13}CH$ from Isotec) and used without further purification. Compounds $[Cp(PPh_3)_2Ru(=C=C=CPh_2)][PF_6]$ (**1**) and its dppe analogues $[Cp(dppe)Ru(=C=C=CPh_2)][PF_6]$ (**1′**) were prepared by following the methods[28] reported in the literature. Infrared

(31) (a) Roth, W. R.; Enderer, K. *Justus Liebigs Ann. Chem.* **1970**, *733*, 44. (b) Wiberg, K. B.; Chen, W. *J. Org. Chem.* **1972**, *37*, 3235. (c) Inoue, Y.; Mukai, T.; Hakushi, T. *Chem. Lett.* **1982**, 1045. (d) Binmore, G. T.; Della, E. W.; Janowski, W. K.; Mallon, P.; Walton, J. C. *Aust. J. Chem.* **1994**, *47*, 1285.

spectra were recorded on a Nicolet-MAGNA-550 spectrometer. The C, H, and N analyses were carried out with a Perkin-Elmer 2400 microanalyzer. Mass spectra (FAB) were recorded using a JEOL SX-102A spectrometer; 3-nitrobenzyl alcohol (NBA) was used as the matrix. NMR spectra were recorded on a Bruker AC-300 instrument at 300 MHz (^{1}H), 121.5 MHz (^{31}P), or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as a standard or an Avance 500 FT-NMR spectrometers.

Synthesis of Complex [Ru]−C≡C−C(Ph)$_2$CH$_2$R (2a, R = CH═CH$_2$). To a 30 mL THF solution of **1** (0.2 g, 0.19 mmol) was added $CH_2CH{=}CH_2MgBr$ (1.0 M in Et_2O; 0.19 mL, 0.19 mmol). The mixture is stirred at −20 °C for 30 min. Then the solution was warmed to room temperature, and the solvent was removed under vacuum. The solid residue was first dissolved in CH_2Cl_2 (5 mL), and then MeOH (15 mL) was added. While the volume of the solvent of the resulting yellow-orange solution was reduced to 5 mL, yellow precipitate formed which was filtered and washed with cold MeOH (2 × 5 mL) and dried under vacuum to give **2a** (yield 85%). Spectroscopic data for **2a**: ^{1}H NMR (C_6D_6): δ 7.75−6.86 (m, 40H, Ph), 6.34 (m, 1H, ═CH), 5.01 (dd, 2H, J_{HH} = 21.0 Hz, J_{HH} = 12.0 Hz, ═CH$_2$), 4.46 (s, 5H, Cp), 3.27 (d, 2H, J_{HH} = 6.0 Hz, CH$_2$). ^{31}P NMR (C_6D_6): δ 51.0. ^{13}C NMR (C_6D_6): δ 149.8−125.4 (m, Ph), 138.2 (s, ═CH), 115.7 (s, ═CH$_2$), 115.1 (s, C$_\beta$), 97.4 (t, J_{CP} = 23.9 Hz, C$_\alpha$), 85.7 (s, Cp), 51.9 (s, C$_\gamma$), 48.0 (s, CH$_2$). Mass *m*/*z* 922.3 (M$^+$), 881.2 (M$^+$ − CH$_2$CH═CH$_2$), 619.2 (M$^+$ − CH$_2$-CH═CH$_2$ − PPh$_3$). IR (KBr, cm^{-1}) ν 2083 (C≡C). Anal. Calcd for $C_{59}H_{50}P_2Ru$: C, 76.85; H, 5.47. Found: C, 76.80; H, 5.57.

Complexes **2b**−**2e** (**2b**, R = CMe═CH$_2$; **2c**, R = C≡CH; **2d**, R = CH$_2$CH═CH$_2$; **2e**, R = Ph) were similarly prepared. Spectroscopic data for **2b** (in 85% yield): ^{1}H NMR (C_6D_6): δ 7.64−6.86 (m, 40H, Ph), 5.10 (s, 1H, ═CH$_2$), 4.97 (s, 1H, ═CH$_2$), 4.48 (s, 5H, Cp), 3.29 (s, 2H, CH$_2$), 1.90 (s, 3H, CH$_3$). ^{31}P NMR (C_6D_6): δ 50.3. ^{13}C NMR (C_6D_6): δ 150.0−125.2 (m, Ph), 143.4 (s, ═CCH$_3$), 115.2 (s, C$_\beta$), 114.6 (s, ═CH$_2$), 96.7 (t, J_{CP} = 24.1 Hz, C$_\alpha$), 51.3 (s, C$_\gamma$), 50.8 (s, CH$_2$), 24.9 (s, CH$_3$). Mass *m*/*z* 936.0 (M$^+$), 881.0 (M$^+$ − CH$_2$CMe═CH$_2$), 691.1 (M$^+$ − C$_2$CPh$_2$CH$_2$CMe═CH$_2$). IR (KBr, cm^{-1}) ν 2082 (C≡C). Anal. Calcd for $C_{60}H_{52}P_2Ru$: C, 76.99; H, 5.60. Found: C, 76.95; H, 5.74.

Spectroscopic data for **2c** (yield 87%): ^{1}H NMR (C_6D_6): δ 7.76−6.87 (m, 40H, Ph), 4.50 (s, 5H, Cp), 3.31 (d, J_{HH} = 2.1 Hz, CH$_2$), 1.74 (t, J_{HH} = 2.1 Hz, C≡CH). ^{31}P NMR (C_6D_6): δ 51.2. ^{13}C NMR (C_6D_6): δ 148.5−125.7 (m, Ph), 114.4 (s, C$_\beta$), 98.6 (t, J_{CP} = 24.1 Hz, C$_\alpha$), 85.6 (s, Cp), 83.5 (s, C≡C), 71.0 (s, ≡CH), 51.4 (s, C$_\gamma$), 34.9 (s, CH$_2$). Mass *m*/*z* 920.0 (M$^+$), 881.0 (M$^+$ − CH$_2$C≡CH), 691.2 (M$^+$ − C$_2$-CPh$_2$CH$_2$C≡CH). IR (KBr, cm^{-1}) ν 2084 (C≡C). Anal. Calcd for $C_{59}H_{48}P_2Ru$: C, 77.02; H, 5.26. Found: C, 77.15; H, 5.31.

Spectroscopic data for **2d** (in 85% yield): ^{1}H NMR (C_6D_6): δ 7.76−6.86 (m, 40H, Ph), 5.90 (m, 1H, ═CH), 4.96 (m, 2H, ═CH$_2$), 4.46 (s, 5H, Cp), 2.58−2.46 (m, 4H, CH$_2$CH$_2$). ^{31}P NMR (C_6D_6): δ 50.9. ^{13}C NMR (C_6D_6): δ 150.2−125.5 (m, Ph), 140.4 (s, ═CH), 115.0 (s, C$_\beta$), 113.8 (s, ═CH$_2$), 97.1 (t, J_{CP} = 23.9 Hz, C$_\alpha$), 52.3 (s, C$_\gamma$), 42.6 (s, CH$_2$), 31.0 (s, CH$_2$). Mass *m*/*z* 936.1 (M$^+$), 881.0 (M$^+$ − CH$_2$CH$_2$-CH═CH$_2$), 691.1 (M$^+$ − C$_2$CPh$_2$CH$_2$CH$_2$CH═CH$_2$). IR (KBr, cm^{-1}) ν 2083 (C≡C). Anal. Calcd for $C_{60}H_{52}P_2Ru$: C, 76.99; H, 5.60. Found: C, 76.95; H, 5.78.

Spectroscopic data for **2e** (in 83% yield): ^{1}H NMR (C_6D_6): δ 7.55−6.84 (m, 45H, Ph), 4.46 (s, 5H, Cp), 3.79 (s, 2H, CH$_2$). ^{31}P NMR (C_6D_6): δ 50.2. ^{13}C NMR (C_6D_6): δ 149.6−125.3 (m, Ph), 114.9 (s, C$_\beta$), 97.8 (t, J_{CP} = 24.1 Hz, C$_\alpha$), 52.9 (s, C$_\gamma$), 49.1 (s, CH$_2$). Mass *m*/*z* 972.4 (M$^+$), 881.3 (M$^+$ − CH$_2$Ph), 691.2 (M$^+$ − C$_2$CPh$_2$CH$_2$Ph). IR (KBr, cm^{-1}) ν 2077 (C≡C). Anal. Calcd for $C_{63}H_{52}P_2Ru$: C, 77.84; H, 5.39. Found: C, 77.98; H, 5.49.

Dppe analogues **2a′**−**2d′** ([Ru] = Cp(dppe)Ru) were also prepared from **1′** and corresponding Grignard reagents using similar methods. Spectroscopic data for **1′**: ^{1}H NMR ($CDCl_3$): δ 7.56−7.00 (m, 30H, Ph); 5.34 (s, 5H, Cp); 2.80 (m, 4H, CH$_2$ of dppe). ^{31}P NMR ($CDCl_3$): δ 82.2. ^{13}C NMR ($CDCl_3$): δ 290.8 (Cα); 204.9 (Cβ); 157.7 (Cγ); 142.7−128.1 (Ph); 91.2 (Cp); 28.5 (CH$_2$ of dppe). MS (FAB) *m*/*z*: 755.2 (M$^+$ − PF$_6$); 565.1 (M$^+$ − PF$_6$, −C$_3$(Ph)$_2$). Anal. Calcd for $C_{46}H_{39}P_3F_6Ru$: C, 61.40; H, 4.36. Found: C, 61.48; H, 4.42.

Spectroscopic data for [Ru]−C≡C−C(Ph)$_2$CH$_2$CH═CH$_2$ (**2a′**, [Ru] = Cp(dppe)Ru, 89% yield): ^{1}H NMR (C_6D_6): δ 8.03−7.06 (m, 30H, Ph); 5.95 (m, 1H, C*H*═CH$_2$); 4.96 (dd, 2H, CH═C*H*$_2$, J_{H-H} = 10.5, 14.3 Hz); 4.92 (s, 5H, Cp); 2.83 (d, 2H, C(Ph)$_2$C*H*$_2$, J_{H-H} = 6.55 Hz); 2.49, 2.13 (m, 4H, CH$_2$ of dppe). ^{31}P NMR (C_6D_6): δ 87.2. ^{13}C NMR (C_6D_6): δ 149.2−125.2 (Ph); 115.1 (CH═*C*H$_2$); 112.2 (C*β*); 98.2 (Cα); 82.6 (Cp); 51.5 (C*γ*); 47.2 (C(Ph)$_2$*C*H$_2$); 27.9 (CH$_2$ of dppe). MS(FAB) *m*/*z*: 796.1 (M$^+$); 565.1 (M$^+$ − C$_3$(Ph)$_2$, CH$_2$CH═CH$_2$). Anal. Calcd for $C_{49}H_{44}P_2Ru$: C, 73.94; H, 5.57. Found: C, 74.02; H, 5.63.

Spectroscopic data for **2b′** (90% yield): ^{1}H NMR (C_6D_6): δ 7.96−7.06 (m, 30H, Ph); 4.94 (s, 5H, Cp); 4.87 (s, 1H, −CH$_2$); 4.61 (s, 1H, −CH$_2$); 2.84 (s, 2H, CH$_2$); 2.28, 1.97 (m, 4H, CH$_2$ of dppe); 1.67 (s, 3H, CH$_3$). ^{31}P NMR (C_6D_6): δ 86.8. ^{13}C NMR (C_6D_6): δ 149.7−112.3 (Ph); 114.1 (−CH$_2$); 112.3 (C$_\beta$); 98.5 (C$_\alpha$); 82.3 (Cp); 51.1 (C$_\gamma$); 49.6 (*C*H$_2$); 27.5 (CH$_2$ of dppe); 24.7 (CH$_3$). MS(FAB) *m*/*z*: 811.2 (M$^+$ + 1); 755.1 (M$^+$ − CH$_2$C(CH$_3$)CH$_2$); 565.1 (M$^+$ − C$_3$(Ph)$_2$CH$_2$C(CH$_3$)-CH$_2$). Anal. Calcd for $C_{49}H_{46}P_2Ru$: C, 73.75; H, 5.81. Found: C, 73.81; H, 5.88.

Spectroscopic data for **2c′** (88% yield): ^{1}H NMR (C_6D_6): δ 8.06−7.06 (m, 30H, Ph); 4.92 (s, 5H, Cp); 2.85 (d, 2H, CH$_2$, J_{H-H} = 2.45 Hz); 2.57, 2.15 (m, 4H, CH$_2$ of dppe); 1.67 (t, 1H, ≡C*H*, J_{H-H} = 2.45 Hz). ^{31}P NMR (C_6D_6): δ 87.4. ^{13}C NMR (C_6D_6): δ 148.1−125.5 (Ph); 112.2 (C$_\beta$); 99.4 (C$_\alpha$); 83.4 (≡C); 82.6 (Cp); 70.3 (≡C); 51.1 (C$_\gamma$); 33.9 (CH$_2$); 28.1 (CH$_2$ of dppe). MS(FAB) *m*/*z*: 794.2 (M$^+$); 755.2 (M$^+$ − CH$_2$C≡CH); 565.1 (M$^+$ − C$_3$(Ph)$_2$, CH$_2$C≡CH). Anal. Calcd for $C_{49}H_{42}P_2Ru$: C, 74.13; H, 5.33. Found: C, 74.19; H, 5.39.

Spectroscopic data for **2d′** (91% yield): ^{1}H NMR (C_6D_6): δ 8.05−7.02 (m, 30H, Ph); 5.96 (m, 1H, ═CH); 5.11 (dd, 2H, ═CH$_2$); 4.91 (s, 5H, Cp); 2.46, 2.18, 2.10 (m, 4H, 2H, 2H, CH$_2$ of dppe, 2CH$_2$). ^{31}P NMR (C_6D_6): δ 87.2. ^{13}C NMR (C_6D_6): δ 149.5−125.1 (Ph); 113.4 (═CH$_2$); 112.3 (C$_\beta$); 97.8 (C$_\alpha$); 82.5 (Cp); 51.7 (C$_\gamma$); 41.7 (CH$_2$); 30.7 (CH$_2$); 27.8 (CH$_2$ of dppe). MS(FAB) *m*/*z*: 810.2 (M$^+$); 755.2 (M$^+$ − CH$_2$CH$_2$CH═CH$_2$); 565.1 (M$^+$ − C$_3$(Ph)$_2$, CH$_2$CH$_2$CH═CH$_2$). Anal. Calcd for $C_{50}H_{46}P_2Ru$: C, 74.14; H, 5.72. Found: C, 74.21; H, 5.80.

Synthesis of Vinylidene Complex {[Ru]═C═CHC(Ph)$_2$CH$_2$R}-BF$_4$ (3a, R = CH═CH$_2$). To a Schlenk flask charged with **2a** (0.1 g, 0.11 mmol) in diethyl ether (15 mL), HBF_4 (54% in Et_2O) was added dropwise at 0 °C under nitrogen. Immediately, a pink precipitate formed, but addition of HBF_4 was continued until no further solid formed. The precipitate was filtered and washed with diethyl ether (2 × 10 mL) and dried under vacuum to give **3a** (yield 95%). Spectroscopic data for **3a**: ^{1}H NMR ($CDCl_3$): δ 7.40−6.92 (m, 40H, Ph), 5.02 (m, 1H, ═CH), 5.00 (s, 5H, Cp), 4.87 (m, 2H, ═CH$_2$), 4.45 (t, 1H, $^4J_{PH}$ = 3.0 Hz, C═CH), 3.06 (s, 2H, J_{HH} = 6.0 Hz, CH$_2$). ^{31}P NMR ($CDCl_3$): δ 42.1. Mass *m*/*z* 923.3 (M$^+$ − BF$_4$), 691.2 (M$^+$ − BF$_4$ − C$_2$HCPh$_2$-CH$_2$CH═CH$_2$). Anal. Calcd for $C_{59}H_{51}BF_4P_2Ru$: C, 70.17; H, 5.09. Found: C, 70.14; H, 5.12.

Complexes **3b**−**3e** (**3b**, R = CMe═CH$_2$; **3c**, R = C≡CH; **3d**, R = CH$_2$CH═CH$_2$; **3e**, R = Ph) were similarly prepared. Spectroscopic data for **3b** (yield 91%): ^{1}H NMR ($CDCl_3$): δ 7.56−6.76 (m, 40H, Ph), 4.99 (s, 5H, Cp), 4.62 (s, 1H, ═CH$_2$), 4.56 (t, 1H, $^4J_{PH}$ = 3.0 Hz, C═CH), 4.53 (s, 1H, ═CH$_2$), 3.10 (s, 2H, CH$_2$), 0.86 (s, CH$_3$). ^{31}P NMR ($CDCl_3$): δ 42.1.

Spectroscopic data for **3c** (yield 94%): ^{1}H NMR ($CDCl_3$): δ 7.41−6.84 (m, 40H, Ph), 5.05 (s, 5H, Cp), 4.81 (t, $^4J_{PH}$ = 3.0 Hz, C═CH), 3.00 (d, $^4J_{HH}$ = 2.1 Hz, CH$_2$), 1.96 (t, $^4J_{HH}$ = 2.1 Hz, C≡CH). ^{31}P NMR ($CDCl_3$): δ 41.5. ^{13}C NMR ($CDCl_3$): δ 346.7 (t, J_{P-C} = 15.1 Hz, C$_\alpha$), 145.7−127.1 (m, Ph), 120.1 (C$_\beta$), 94.5 (Cp), 81.1 (C≡CH), 72.6 (≡CH), 50.5 (C$_\gamma$), 33.4 (CH$_2$). Mass *m*/*z* 920.0 (M$^+$ − 1 − BF$_4$), 691.0 (M$^+$ − BF$_4$ − C$_2$HCPh$_2$CH$_2$C≡CH). Anal. Calcd. for $C_{59}H_{49}$-BF_4P_2Ru: C, 70.31; H, 4.90. Found: C, 70.38; H, 5.08.

Spectroscopic data for **3d** (yield 96%): ^{1}H NMR ($CDCl_3$): δ 7.41−6.81 (m, 40H, Ph), 5.69 (m, 1H, ═CH), 5.00 (s, 5H, Cp), 4.90 (s, 2H, ═CH$_2$), 4.59 (t, 1H, $^4J_{PH}$ = 3.0 Hz, C═CH), 2.36 (m, 2H, CH$_2$), 1.54

(m, 2H, CH_2). ^{31}P NMR ($CDCl_3$): δ 41.8. ^{13}C NMR ($CDCl_3$): δ 347.5 (t, J_{P-C} = 15.1 Hz, C_α), 146.7−126.7 (Ph), 137.7 (=CH), 120.2 (=CH_2), 115.0 (C_β), 94.2 (Cp), 50.9 (C_γ), 41.0, (CH_2), 29.2 (CH_2). Mass *m*/*z* 936.1 ($M^+ - 1 - BF_4$), 691.1 ($M^+ - BF_4 - C_2HCPh_2CH_2CH_2$-$CH{=}CH_2$). Anal. Calcd for $C_{60}H_{53}BF_4P_2Ru$: C, 70.38; H, 5.22. Found: C, 70.43; H, 5.20.

Spectroscopic data for **3e** (yield 93%): ^1H NMR ($CDCl_3$): δ 7.39−6.39 (m, 45H, Ph), 4.96 (s, 5H, Cp), 4.10 (t, 1H, $^4J_{PH}$ = 3.0 Hz, C=CH), 3.65 (s, 2H, CH_2). ^{31}P NMR ($CDCl_3$): δ 42.0. ^{13}C NMR ($CDCl_3$): δ 346.8 (t, J_{P-C} = 15.1 Hz, C_α), 147.0−126.8 (Ph), 118.7 (C_β), 94.7 (Cp), 53.0 (C_γ), 49.2, (CH_2). Mass *m*/*z* 973.1 ($M^+ - BF_4$), 881.1 ($M^+ - BF_4 - CH_2Ph$), 691.0 ($M^+ - BF_4 - C_2HCPh_2CH_2Ph$). Anal. Calcd for $C_{63}H_{53}BF_4P_2Ru$: C, 71.39; H, 5.04. Found: C, 71.43; H, 5.11.

Complexes **3a′**, **3c′**, and **3d′** were also prepared using similar procedures. Spectroscopic data for **3a′** (96% yield): ^1H NMR ($CDCl_3$): δ 7.47−6.67 (m, 30H, Ph); 5.84 (m, 1H, =CH); 5.23 (s, 5H, Cp); 4.83 (m, 1H, $=CH_2$); 3.45 (s, 1H, C=CH); 2.73 (m, 4H, CH_2 of dppe); 2.27 (d, 2H, $CH_2C(Ph)_2$). ^{31}P NMR ($CDCl_3$): δ 77.6. Complex **3b′** was not obtained. Upon protonation of **2b′** complex **6b′** was directly obtained in 97% yield.

Spectroscopic data for **3c′** (95% yield): ^1H NMR ($CDCl_3$): δ 7.50−6.69 (m, 30H, Ph); 5.39 (s, 5H, Cp); 4.96 (s, 1H, CH); 3.75 (s, 1H, $CHC(Ph)_2$); 2.80 (m, 4H, CH_2 of dppe); 2.15 (d, 2H, CH_2; J_{H-H} = 2.4 Hz); 1.94 (t, 1H, ≡CH, J_{H-H} = 2.4 Hz). ^{31}P NMR ($CDCl_3$): δ 77.5. ^{13}C NMR ($CDCl_3$): δ 343.2 (t, Cα, J_{P-C} = 15.5 Hz); 145.9−126.7 (Ph); 120.9 (C_β); 91.8 (Cp); 81.3 (≡C); 72.4 (≡CH); 49.7 (C_γ); 31.8 (CH_2); 26.9 (CH_2 of dppe). MS(FAB) *m*/*z*: 795.2 (M^+); 755.2 (M^+ − 1, $-CH_2C{\equiv}CH$); 565.1 ($M^+ - C_3H(Ph)_2$, $CH_2C{\equiv}CH$). Anal. Calcd for $C_{49}H_{43}P_2BF_4Ru$: C, 66.75; H, 4.91. Found: C, 66.82; H, 4.98.

Spectroscopic data for **3d′** (93% yield): ^1H NMR ($CDCl_3$): δ 7.51−6.56 (m, 30H, Ph); 5.52 (m, 1H, =CH); 5.32 (s, 5H, Cp); 4.89 (d, 1H, $=CH_2$, J_{H-H} = 8.1 Hz); 4.83 (d, 1H, $=CH_2$, J_{H-H} = 17.2 Hz); 3.68 (s, 1H, CH); 2.83, 2.58 (m, 4H, CH_2 of dppe); 1.56 (br, 4H, $2CH_2$). ^{31}P NMR ($CDCl_3$): δ 77.8. ^{13}C NMR ($CDCl_3$): δ 341.5 (t, C_α); 147.1−126.0 (Ph); 120.8 (C_β); 114.6 ($=CH_2$); 91.5 (Cp); 51.4 (C_γ); 39.9 (CH_2); 29.5 (CH_2); 26.7 (CH_2 of dppe). MS(FAB) *m*/*z*: 811.2 (M^+); 755.2 ($M^+ - CH_2CH_2CH{=}CH_2$); 565.1 ($M^+ - C_3H(Ph)_2$, $CH_2CH_2CH{=}CH_2$). Anal. Calcd for $C_{50}H_{47}P_2BF_4Ru$: C, 66.89; H, 5.27. Found: C, 66.93; H, 5.31.

Preparation of Complex {[Ru]=C=CHCH$_2$C(Ph)$_2$CH=CH$_2$}-BF$_4$ (4a). A Schlenk flask was charged with **3a** (0.1 g, 0.11 mmol) and CH_2Cl_2 (15 mL). The solution was heated to reflux under nitrogen for 4 h and then cooled to room temperature. The solvent was reduced to 5 mL under vacuum, and then the residual mixture was added to 30 mL of diethyl ether. The orange precipitate thus formed was filtered and washed with diethyl ether (2 × 10 mL) and dried under vacuum to give **4a** (yield 90%). Spectroscopic data for **4a**: ^1H NMR ($CDCl_3$): δ 7.41−6.78 (m, 40H, Ph), 6.51 (dd, 1H, J_{HH} = 18.0, 10.8 Hz, =CH), 5.29 (d, 1H, J_{HH} = 10.8 Hz, $=CH_2$), 4.87 (s, 5H, Cp), 4.71 (d, 2H, J_{HH} = 18.0 Hz, $=CH_2$), 4.40 (m, 1H, C=CH), 3.09 (d, 2H, J_{HH} = 7.8 Hz, CH_2). ^{31}P NMR ($CDCl_3$): δ 43.9. ^{13}C NMR (C_6D_6): δ 345.6 (t, J_{P-C} = 15.1 Hz, C_α), 145.4−126.6 (Ph), 143.7 (=CH), 115.3 ($=CH_2$), 110.5 (s, C_β), 94.4 (s, Cp), 54.0 (s, C_γ), 31.9 (s, CH_2). Mass *m*/*z* 923.3 ($M^+ - BF_4$), 691.2 ($M^+ - BF_4 - C_2H\ CH_2CPh_2CH{=}CH_2$). Anal. Calcd for $C_{59}H_{51}BF_4P_2Ru$: C, 70.17; H, 5.09. Found: C, 70.19; H, 5.15.

Thermolysis of 3a in Acetonitrile. Complex **3a** (0.1 g, 0.11 mmol) was dissolved in 15 mL of CH_3CN at room temperature. The solution was heated to reflux for 1 h under nitrogen. Solvent was then removed under vacuum. The solvent was reduced to 5 mL under vacuum, and then the residual mixture was added to 30 mL of diethyl ether. The pale-orange precipitate thus formed was filtered and washed with diethyl ether (2 × 10 mL) and dried under vacuum to give {[Ru]$NCCH_3$}BF_4. The filtrate was evaporated to dryness, and the crude product was purified by column chromatography on silica gel with hexanes as eluent. Evaporation of the solvent gave a mixture of terminal enyne **7a** and **8a** as a colorless oil (yield 87%). Spectroscopic data of **7a** are consistent with that of literature data.

Preparation of 8a. A Schlenk flask was charged with **4a** (0.1 g, 0.11 mmol) and CH_3CN (15 mL). The solution was heated to reflux under nitrogen for 1 h and then cooled to room temperature. The solvent was reduced to 5 mL under vacuum, and then the residual mixture was added to 30 mL of diethyl ether. The pale-orange precipitate thus formed was filtered and washed with diethyl ether (2 × 10 mL) and dried under vacuum to give {[Ru]$NCCH_3$}BF_4. The filtrate was evaporated to dryness, and crude product was purified by column chromatography on silica gel with hexanes as eluent. Evaporation of the solvent gave terminal enyne **8a** as a colorless oil (yield 77%). Spectroscopic data for **8a**: ^1H NMR ($CDCl_3$): δ 7.31−7.19 (m, 10H, Ph), 6.52 (dd, 1H, J_{HH} = 17.7 Hz, J_{HH} = 10.8 Hz, =CH), 5.28 (d, 1H, J_{HH} = 10.8 Hz, $=CH_2$), 4.86 (d, 1H, J_{HH} = 17.7 Hz, $=CH_2$), 3.12 (d, 2H, J_{HH} = 2.4 Hz, CH_2), 1.90 (t, 1H, J_{HH} = 2.4 Hz, ≡CH). ^{13}C NMR ($CDCl_3$): δ 145.1 (s, Ph), 143.8 (s, =CH), 128.5 (s, Ph), 128.2 (s, Ph), 126.5 (s, Ph), 115.3 (s, $=CH_2$), 81.6 (s, ≡C), 71.5 (s, ≡CH), 53.5 (s, CPh_2), 30.1 (s, CH_2).

Conversion of 3a′ to 4a′. Complex **3a′** (90 mg, 0.113 mmol) was dissolved in 10 mL of CH_2Cl_2 and stirred for 1 h at room temperature. Then diethyl ether was added, and **5a** was precipitated as an orange solid which was filtered and washed with ether and dried under vacuum to give **4a′** (85 mg, 0.106 mmol) in 93% yield. Spectroscopic data for **4a′**: ^1H NMR ($CDCl_3$): δ 7.67−6.70 (m, 30H, Ph); 6.00 (m, 1H, =CH, J_{H-H} = 10.8, 16.8 Hz); 5.22 (s, 5H, Cp); 5.03 (d, 1H, $=CH_2$, J_{H-H} = 10.7 Hz); 4.43 (d, 1H, $=CH_2$, J_{H-H} = 17.5 Hz); 3.20 (t, 1H, C=CH, J_{H-H} = 7.25 Hz); 2.76 (m, 4H, CH_2 of dppe); 2.21 (d, 2H, CH_2, J_{H-H} = 7.25 Hz). ^{31}P NMR ($CDCl_3$): δ 87.2. ^{13}C NMR ($CDCl_3$): δ 341.7 (t, C_α, J_{P-C} = 16.3 Hz); 145.2−126.2 (Ph); 114.5 (C_β); 108.5 ($=CH_2$); 91.4 (Cp); 53.2 (C_γ); 28.7 (CH_2); 27.3 (CH_2 of dppe). MS (FAB) *m*/*z*: 796.1 (M^+ − 1); 565.1 (M^+ − 1, $-C_3(Ph)_2$, CH_2CHCH_2). Anal. Calcd for $C_{49}H_{45}P_2BRuF_4$: C, 66.59; H, 5.13. Found: C, 66.62; H, 5.18.

Preparation of 6b. A Schlenk flask was charged with **3b** (0.10 g, 0.10 mmol) and CH_2Cl_2 (15 mL) under nitrogen. The solution was stirred at room temperature for 1 min. The solvent was reduced to 5 mL under vacuum, and then 30 mL of diethyl ether were added to give an orange precipitate which was filtered and washed with diethyl ether (2 × 10 mL) and dried under vacuum to give **6b** (yield 83%). Spectroscopic data for **6b**: ^1H NMR (CD_2Cl_2): δ 7.58−6.30 (m, 40H, Ph), 5.39 (br, 1H, =CH), 4.96 (s, 5H, Cp), 2.76 (d, J_{HH} = 14.0 Hz, 1H of CH_2), 2.70 (t, J_{P-H} = 10.0 Hz, br, 1H, =CH), 1.66 (m, 1H, CH), 1.56 (d, J_{HH} = 5.5 Hz, CH_3 + 1H of CH_2). ^{31}P NMR ($CDCl_3$): δ 41.3, 40.9 (d, J_{P-P} = 36.4 Hz, 2 PPh_3). ^{13}C NMR (CD_2Cl_2, 258K): δ 151.1−125.5 (Ph), 144.7 (dd, J_{P-C} = 22.6, 2.5 Hz, =C=), 131.6 (=CH); 90.4 (Cp), 57.7 (CPh_2), 51.2 (CH_2), 43.4 (=CH), 35.2 (=CH), 20.3 (CH_3). Mass *m*/*z* 937.1 ($M^+ - BF_4$), 675.1 ($M^+ - BF_4 - PPh_3$). Anal. Calcd for $C_{60}H_{53}BF_4P_2Ru$: C, 70.38; H, 5.22. Found: C, 70.29; H, 5.17.

Spectroscopic data for **6b′**: ^1H NMR ($CDCl_3$): δ 7.68−6.65 (m, 30H, Ph); 5.04 (s, 5H, Cp); 4.96 (s, 1H, CH); 3.25, 2.70, 2.62, 2.25 (m, 4H, CH_2 of dppe); 2.40, 1.42 (m, 2H, $C(Ph)_2CH_2$); 1.17 (m, 1H, CH); 1.14 (m, 1H, CH); 0.82 (d, J_{H-H} = 7.9 Hz, 3H, CH_3). ^{31}P NMR ($CDCl_3$): δ 78.1, 74.2 (AX, J_{P-P} = 25.1 Hz). ^{13}C NMR ($CDCl_3$): δ 151.1−126.4 (Ph); 143.5 (d, J_{P-C} = 24.8 Hz, =C=); 132.7 (=CH); 90.6 (Cp); 58.1 (CPh_2); 51.2 (CH_2); 43.2 ($C(CH_3)$); 32.9 (=CH); 27.5, 24.8 (CH_2 of dppe); 19.2 (CH_3). MS (FAB) *m*/*z*: 811.2 ($M^+ - BF_4$); 565.1 ($M^+ - BF_4$, $C_3(Ph)_2CH_2C(CH_3)CH_2$). Anal. Calcd for $C_{49}H_{47}P_2$-BF_4Ru: C, 66.44; H, 5.34. Found: C, 66.49; H, 5.41.

Preparation of 4c. A Schlenk flask was charged with **3c** (0.1 g, 0.10 mmol) and $CHCl_3$ (10 mL)/CH_2Cl_2 (5 mL) under nitrogen. The resulting solution was heated to reflux for 4 h and then cooled to room temperature. The solvent was reduced to 5 mL under vacuum, and the mixture was added to 30 mL of diethyl ether. The gray precipitate thus formed was filtered and washed with diethyl ether (2 × 10 mL) and dried under vacuum to give **4c** (yield 74%). Spectroscopic data for **4c**:

^{1}H NMR ($CDCl_3$): δ 7.77−6.79 (m, 40H, Ph), 4.83 (s, 5H, Cp), 4.67 (m, 1H, C═CH), 3.09 (d, J_{HH} = 7.8 Hz, CH_2), 2.78 (s, ≡CH). ^{31}P NMR ($CDCl_3$): δ 43.8. Mass *m*/*z* 921.1 ($M^+ - BF_4$), 691.1 ($M^+ - BF_4 - C_2HCH_2CPh_2C{\equiv}CH$). Anal. Calcd for $C_{59}H_{49}BF_4P_2Ru$: C, 70.31; H, 4.90. Found: C, 70.37; H, 5.03.

The same reaction in CH_3CN for 1 h gave $[Ru]NCCH_3^+$ and $HC{\equiv}CC(Ph)_2CH_2C{\equiv}CH$, **9c**. Two products were separated by the method used for the separation of **8a** and $[Ru]NCCH_3^+$. Spectroscopic data for **9c** (yield 83%): ^{1}H NMR ($CDCl_3$): δ 7.49−7.21 (m, 10H, Ph), 3.16 (d, 1H, J_{HH} = 2.4 Hz, ≡CH), 2.66 (s, 1H, ≡CH), 2.01 (t, 1H, J_{HH} = 2.4 Hz, CH_2). ^{13}C NMR ($CDCl_3$): δ 143.3 (s, Ph), 128.3 (s, Ph), 127.4 (s, Ph), 127.1 (s, Ph), 87.2 (s, ≡C), 80.7 (s, ≡C), 73.9 (s, ≡CH), 71.4 (s, ≡CH), 48.9 (s, CPh_2), 32.7 (s, CH_2).

Single-Crystal X-ray Diffraction Analysis of 6b. Single crystals of **6b** suitable for an X-ray diffraction study were grown as mentioned above. A single crystal of dimensions 0.25 × 0.20 × 0.15 mm^3 was glued to a glass fiber and mounted on an SMART CCD diffractometer. The diffraction data were collected using 3 kW sealed-tube Mo Kα radiation (T = 295 K). Exposure time was 5 s per frame. SADABS[32] (Siemens area detector absorption) absorption correction was applied, and decay was negligible. Data were processed, and the structure was solved and refined by the SHELXTL[33] program. The structure was solved using direct methods and confirmed by Patterson methods refining on intensities of all data (33 919 reflections) to give R1 = 0.0584 and wR2 = 0.1370 for 11 445 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.

Acknowledgment. This research is supported by the National Science Council of Taiwan, the Republic of China. Valuable suggestions on the mechanism from Professor Kung Wang of West Virginia University and Professor Charles P. Casey of University of Wisconsin at Madison are gratefully acknowledged.

Supporting Information Available: Complete crystallographic data for **6b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA054994A

(32) The SADABS program is based on the method of Blessing; see: Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33−38.

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