

η^1 -Vinylidene Formation from Internal Alkynones by C–C Bond MigrationMichael J. Shaw,^{*,[a]} Steven W. Bryant,^[a] and Nigam Rath^[b]**Keywords:** Ruthenium / Alkynes / Isomerization / Vinylidene bond activation / Unsaturated complexes

The $[\mu^2\text{-N}_2\{\text{CpRu}(\text{PPh}_3)_2\}_2]^{2+}$ (1^{2+}) dication is a source of the formal 16-electron $[\text{CpRu}(\text{PPh}_3)_2]^+$ fragment, and it reacts with internal alkynes such as 1,3-diphenylpropyne, 4-phenyl-3-butyne-2-one, and 3-cyclopropyl-1-phenylpropyne to yield η^1 -vinylidene complexes $2\mathbf{a}^+$ – $2\mathbf{c}^+$ by C–C bond activation. In the case of 1,3-diphenylpropyne, the η^1 -ketone complex $[\text{CpRu}(\text{PPh}_3)_2\{\text{PhC}(\eta^1\text{-O})\text{C}\equiv\text{CPh}\}]^+$ ($3\mathbf{a}^+$) was isolated as its PF_6^- salt, and it is apparently an intermediate in the formation of the vinylidene complex.

Complexes $2\mathbf{a}^+$ – $2\mathbf{c}^+$ were characterized as their $\text{BAR}_4^{\text{F}-}$ [$\text{ArF} = 3,5\text{-bis(trifluoromethyl)phenyl}$] salts by NMR and IR spectroscopic methods, ESI-MS, and EA. The single crystal X-ray diffraction structure of $2\mathbf{a}\text{BAR}_4^{\text{F}}$ is presented. These reactions represent the first examples where an internal alkyne undergoes C–C bond migration to form an η^1 -vinylidene complex.

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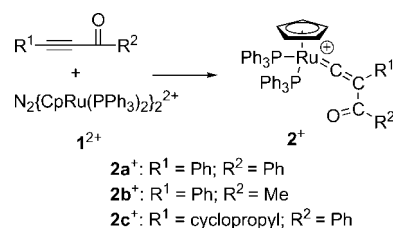
Introduction

Terminal vinylidene complexes have an established role in the catalytic and stoichiometric transformation of alkynes into elaborated structures.^[1] The isomerization of alkyne ligands to vinylidenes has been examined in detail by experimental^[2] and theoretical techniques^[3] and this reaction continues to generate interest.^[4] A net 1,2-H atom shift is common,^[5] but the migration of other functional groups is limited to $-\text{SiMe}_3$, $-\text{SR}$, and $-\text{I}$,^[1,6] which means that further reactions are necessary to produce disubstituted vinylidenes. In only one case has C–C bond activation been observed in an alkyne-to-vinylidene conversion,^[7] although C–C bond migration in vinylidene-to-alkyne isomerization has been reported.^[8] This communication details the formation of terminal vinylidene complexes through C–C bond activation of acetylenic ketones by electrophilic cations derived from $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$, a well-known starting material for the formation of vinylidene ligands from terminal alkynes.^[9]

Results and Discussion

Halide abstraction of Cl^- by silver salts from $[\text{CpRu}(\text{L})_2\text{Cl}]$ ($\text{L} = \text{phosphane}$) results in the formation of unsaturated cationic complexes that absorb N_2 even from high-purity argon.^[10a] Thus, a solution that behaves as

“ $[\text{CpRu}(\text{PPh}_3)_2]\text{PF}_6$ ” can be prepared in situ from $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$ and AgPF_6 in CH_2Cl_2 , but the actual metal species has proved difficult to isolate and characterize, a circumstance previously described for several related unsaturated metal complexes.^[10] A tractable material that serves as a synthon for the “ $[\text{CpRu}(\text{PPh}_3)_2]^+$ ” unit is $[\mu^2\text{-N}_2\{\text{CpRu}(\text{PPh}_3)_2\}_2](\text{BAR}_4^{\text{F}})_2$ ($1(\text{BAR}_4^{\text{F}})_2$, $\text{ArF} = 3,5\text{-bis(trifluoromethyl)phenyl}$). The addition of 1,3-diphenylpropyne, 4-phenyl-3-butyne-2-one, or 3-cyclopropyl-1-phenylpropyne to CH_2Cl_2 or CDCl_3 solutions of $1(\text{BAR}_4^{\text{F}})_2$ immediately and cleanly yield the η^1 -vinylidene complexes $2\mathbf{a}\text{BAR}_4^{\text{F}}$ – $2\mathbf{c}\text{BAR}_4^{\text{F}}$, respectively (Scheme 1).



Scheme 1. Formation of vinylidene complexes from acetylenic ketones.

The single-crystal X-ray diffraction study (Figure 1)^[11] of $2\mathbf{a}\text{BAR}_4^{\text{F}}$ reveals the vinylidene cation $2\mathbf{a}^+$ and clearly shows that an unexpected C–C bond migration has taken place. This rearrangement represents an unprecedented rearrangement for an internal alkyne in a monometallic compound.

The structure of $2\mathbf{a}^+$ is comparable to similar structures of $[\text{CpRu}(\text{L})_2(\text{vinylidene})]^+$ cations ($\text{L} = \text{phosphane}$) with a $\text{Ru}=\text{C}$ bond length of 1.818(4) Å, a $\text{C}=\text{C}$ bond length of 1.335(5) Å, and $\text{P}-\text{Ru}-\text{C}$ bond angles of 94.65(11)° and 98.30(3)°.^[12] This structure clearly establishes that C–C bond migration occurs, which transforms 1,3-diphenylpro-

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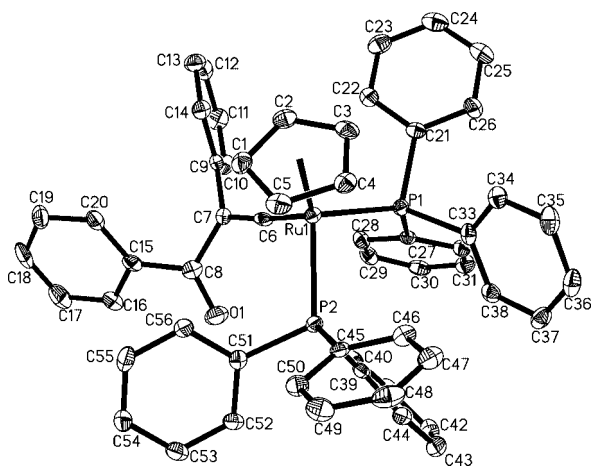


Figure 1. Projection view of complex **2a**⁺ with 50% thermal ellipsoids. The counterion and H atoms are omitted for clarity.

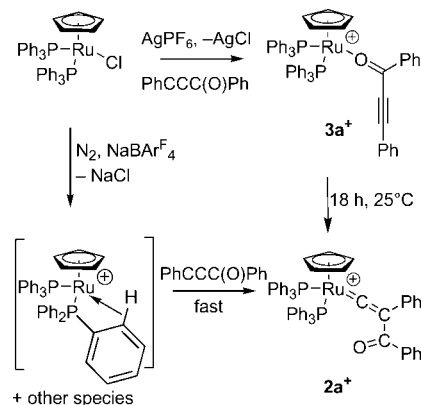
pynone into the 2-phenyl-2-benzoylvinylidene ligand. Cation **2a**⁺ is close in size to the BARF_4^- anion (Supporting Information, Figure S1), a factor that often aids in the crystallization process. The solubility of the BARF_4^- salts in CDCl_3 and Et_2O is higher than the corresponding PF_6^- salts, which tend to form oily masses rather than X-ray quality crystals.

Complexes **2a**⁺–**2c**⁺ were spectroscopically characterized by ^1H , ^{13}C , ^{31}P , and ^{19}F NMR spectroscopy, IR spectroscopy, and ESI-MS as their BARF_4^- salts. For example, the NMR spectra of **2aBARF**₄ show the expected features such as a single resonance due to the C_5H_5 group in the ^1H and ^{13}C NMR spectra, and a single resonance due to the two equivalent phosphane ligands and the BARF_4^- anion, respectively, in the ^{31}P and ^{19}F NMR spectra. Of note is the resonance at $\delta = 349.53$ ppm in the ^{13}C NMR spectrum, which is due to the vinylidene carbon atom attached directly to the Ru atom.^[13] Similarly, terminal vinylidenes **2bBARF**₄ and **2cBARF**₄ show diagnostic peaks in the ^{13}C NMR spectra at 351.91 and 353.29 ppm, respectively (see Supporting Information). For **2aBARF**₄, a feature in the IR spectrum at 1658 cm^{-1} is attributed to the vinylidene stretching vibration,^[12b] but this vibration also appears to couple with the ketone stretching frequency that should occur in a similar position. The ESI-MS spectrum of **2aBARF**₄ reveals the P^+ peak at 897 m/z with the expected pattern of Ru-isotope peaks.

The nature of the “[CpRu(PPh₃)₂]⁺” cation in these reactions is an important factor. Solid samples of **1**(BARF_4)₂ can be prepared by treating [CpRu(PPh₃)₂Cl] with NaBARF₄ in CH_2Cl_2 under an argon atmosphere, followed by filtration of the mixture to remove NaCl and recrystallization (see Supporting Information). The Raman spectra of solid samples of **1**(BARF_4)₂ show a peak at 2062 cm^{-1} , which is due to the bridging N_2 ligand.^[10a,14] Exposure of this material in solution to nitrogen gas results in a band at 2192 cm^{-1} in the KBr-pellet IR spectrum of the resulting solid as a result of the formation of a terminal N_2 ligand.^[10a,14] However, exposure to excess N_2 appears to have no effect on the reac-

tions of isolated **1**(BARF_4)₂ with alkynes. Additionally, a CH_2Cl_2 signal ($\delta = 5.32$ ppm) is observed in the ^1H NMR spectrum of samples of **1**(BARF_4)₂, so this solid is formulated as **1**(BARF_4)₂· CH_2Cl_2 , which is consistent with the microanalytical data. As yet, X-ray quality crystals of this material are not available.

In CDCl_3 solution, **1**(BARF_4)₂ appears to change into two species. As expected, there is no evidence of interaction between the noncoordinating BARF_4^- anion and cation **1**²⁺ in the ^{19}F NMR spectrum. The ^1H NMR spectra of **1**(BARF_4)₂ in CDCl_3 reveal two broad resonances at 4.53 and 5.16 ppm attributable to C_5H_5 protons, which indicates that the bulk of the ruthenium complex exists in two forms. There are also broad ^1H NMR signals at 7.01 and 10.11 ppm assigned to the *ortho* hydrogen atoms of the PPh₃ ligands. The ^1H NMR signal at 10.11 ppm disappears upon addition of alkyne with a corresponding increase in the usual Ph region of the spectrum. We suggest that the 10.11 ppm signal indicates that some of the ruthenium complex converts to a monometallic species agostically stabilized in solution by *ortho* C–H interactions as depicted in Scheme 2. Crystallographically characterized examples of related complexes with and without agostic interactions are known.^[15] It is unlikely that this second cation exists as a true 16-electron species, as such compounds are known to have intense blue color.^[14]



Scheme 2. The reaction of 1,3-diphenylpropyne with **1** BARF_4 and in-situ-generated 1PF_6 .

The reaction conditions play a considerable role in this alkyne-to-vinylidene conversion. Solutions of **1**(BARF_4)₂ under an atmosphere of argon react immediately with 1,3-diphenylpropyne to form **2aBARF**₄. Solutions of “CpRu(PPh₃)₂PF₆” generated in situ under an atmosphere of N_2 react over several hours to yield a mixture of products, in which **2aPF**₆ can be observed spectroscopically by IR and ^1H NMR spectroscopy. Under these conditions an additional isomer of **2aPF**₆ can be isolated (Scheme 2). The η^1 -ketone complex **3aPF**₆ can be isolated as a red-brown powder by fractional crystallization at -30°C . Compound **3aPF**₆ was characterized by NMR and IR spectroscopic methods and ESI-MS. These data establish that cation **3a**⁺ is an isomer of **2a**⁺. The definitive evidence for the η^1 -ketone structure of **3aPF**₆ comes from its IR spectrum

where an alkyne band at 2202 cm^{-1} is almost unchanged from that of 1,3-diphenylpropynone (2207 cm^{-1}), whereas the ketone band moves to 1524 cm^{-1} , a shift of 116 cm^{-1} lower than that of the free ligand.^[16] The ^{13}C NMR spectra support this assignment with alkyne C atoms observable in their usual range, and the carbonyl C atom resonates at almost the same chemical shift as in the free ligand.^[16]

It thus appears that the presence of ligands that coordinate more strongly than BAR^{F_4-} (such as PF_6^-) is a factor that can slow the formation of the vinylidene cation. CH_2Cl_2 solutions of “[$\text{CpRu}(\text{PPh}_3)_2$] PF_6 ” generated in situ by halide abstraction and then exposed to N_2 slowly develop IR bands at 2181 cm^{-1} , which are due to terminal N_2 ligands, as previously observed for similar Ru species.^[14] The addition of 1,3-diphenylpropynone to such solutions (Scheme 2) immediately induces a change in the burgundy of 3aPF_6 . Over a period of hours, the color reverts to orange-brown. Progress monitored by FTIR spectroscopy indicates the immediate conversion of some “[$\text{CpRu}(\text{PPh}_3)_2$] PF_6 ” into 3aPF_6 , as evidenced by the appearance of a strong IR band at 1532 cm^{-1} . However, the alkyne band and the bound ketone band are very slowly consumed, whereas features due to vinylidene complex 2aPF_6 increase in intensity (see Supporting Information). No features due to an η^2 -alkyne complex are observed in the region 1800 – 2000 cm^{-1} . From these results it is clear that the ketone complex 3aPF_6 slowly isomerizes in CH_2Cl_2 to form the vinylidene complex 2aPF_6 .

An η^2 -alkyne intermediate cannot be ruled out at present. The conversion of η^1 -ketone to η^2 -alkyne complexes was previously observed and is facile.^[17] Calculations on [$\text{Cp}(\text{PMe}_3)_2(\eta^2\text{-HC}\equiv\text{CR})$] $^+$ ($\text{R} = \text{H}, \text{CH}_3$) complexes show that initial slippage of the Ru atom from the alkyne triple bond to the terminal C–H bond is a necessary step in the isomerization process.^[14d] It is likely that activation of the C(O)R group occurs in these reactions by a similar interaction of the Ru atom with the C–C bond that links the alkyne to the C=O unit. Ph group migration is unlikely because the addition of diphenylacetylene to 1BAR^{F_4} yields no vinylidene (monitored by NMR spectroscopy) and at least one related $\eta^2\text{-PhC}\equiv\text{CPh}$ complex was crystallographically characterized.^[18] In the formation of the cyclopropyl complex $2\text{cBAR}^{\text{F}_4}$, no sign of ring-opening occurs during isomerization. If the cyclopropyl ring migrates, then migration must occur without a significant amount of positive charge or unpaired electron density build up on the migrating group, as these factors would encourage ring opening. Detailed calculations on this reaction pathway are currently underway.

Conclusions

This report describes the reaction of an internal alkyne with a commonly encountered d^6 -Ru complex cation that results in C–C bond migration to form a vinylidene complex. This migration represents a new path to disubstituted terminal vinylidene complexes, which are currently of in-

tense theoretical and applied interest, and it may represent a general method for the activation of internal alkynes found in acetylenic ketones. Further theoretical and experimental studies are underway to establish a pathway for the activation of the acetylenic ketone ligand.

Experimental Section

All manipulations were carried out under an atmosphere of pre-purified nitrogen or argon. All solvents were distilled from appropriate drying agents (e.g. CaH_2 or K) and freeze–pump–thaw degassed before use.

Preparation of $2\text{aBAR}^{\text{F}_4}$: Under an atmosphere of dry argon, [$\text{CpRu}(\text{PPh}_3)_2\text{Cl}$] (1.40 g, 1.93 mmol) was mixed with AgPF_6 (0.487 g, 1.78 mmol) in CH_2Cl_2 (50 mL). The solution was stirred for 30 min and then 1,3-diphenylpropynone (0.45 g, 2.18 mmol) was added. The mixture was stirred in the dark for 5 d whereupon it was filtered, concentrated, and cooled to -30°C . After 2 d, white crystals of AgCl had formed, and the solution was transferred to another vessel, further concentrated, and cooled again to -30°C . This procedure was repeated until no more white precipitate formed, and then a crude solid (1.30 g) was precipitated from the solution by the addition of Et_2O (50 mL). Half of the crude solid (0.62 g) was dissolved in CH_2Cl_2 (2.0 mL) to which $\text{NaBAR}^{\text{F}_4}$ (0.61 g, 0.69 mmol) was added. The solution was stirred for 30 min, filtered, and Et_2O (10 mL) was added. The solution was concentrated under reduced pressure and cooled to -30°C overnight whereupon $2\text{aBAR}^{\text{F}_4}$ precipitated from the solution as bright-orange crystals that were suitable for x-ray diffraction studies. Further concentration of the mother liquor resulted in four more crops of $2\text{aBAR}^{\text{F}_4}$ {0.521 g total, estimate 15% yield based on original [$\text{CpRu}(\text{PPh}_3)_2\text{Cl}$]}. ^1H NMR (300 MHz, CDCl_3 , 25°C): $\delta = 5.12$ (s, C_5H_5), 6.80–7.78 (m, aromatic) ppm. ^{13}C NMR (75 MHz, CDCl_3 , 25°C): $\delta = 349.53$ (s, $\text{Ru}=\text{C}=\text{C}$), 188.57 (s, $\text{C}=\text{O}$), 95.29 (s, C_5H_5), 82.00 (s, $\text{Ru}=\text{C}=\text{C}$) ppm. ^{31}P NMR (121.46 MHz, CDCl_3 , 25°C): $\delta = 40.48$ (s) ppm. IR (KBr): $\tilde{\nu} = 1657, 1557, 1439, 1360, 1281, 1128\text{ cm}^{-1}$. ESI-MS: $m/z = 987$ [$\text{P} - \text{BAR}^{\text{F}_4}$] $^+$. [$\text{C}_{88}\text{H}_{57}\text{BF}_{24}\text{OP}_2\text{Ru}$] (1760.21): calcd. C 60.05, H 3.26; found C 60.07, H 3.28.

Preparation of 3aPF_6 : [$\text{CpRuCl}(\text{PPh}_3)_2$] (0.38 g, 0.50 mmol), CH_2Cl_2 (20 mL), and AgPF_6 (0.13 g, 0.50 mmol) were placed in a 100-mL Schlenk tube. The mixture was stirred under inert conditions, and a voluminous white precipitate formed. The mixture was stirred for 30 min and 1,3-diphenylpropynone (0.11 g, 0.50 mmol) was then added. The mixture was stirred overnight in the dark and then filtered through a 1-cm layer of Celite supported on a medium porous glass frit. Toluene (2 mL) was then added to induce crystallization, and the mixture was concentrated under reduced pressure. The solution was cooled overnight to -30°C , and a small amount of solid was isolated. Three small crops of solid were obtained first, all between ca. 2 and 5 mg, which corresponded to impure AgCl and 1PF_6 . After these crops were obtained, the solution began to form a separate layer of oil. The oil was concentrated under reduced pressure and Et_2O was added (10 mL), and the solution was stirred overnight. The resulting powder of 3PF_6 (0.22 g, 42%) was isolated by filtration, rinsed with Et_2O , and dried under vacuum. ^1H NMR (300 MHz, CDCl_3): $\delta = 6.9$ – 7.6 (40 H, Ph), 5.22 (5 H, C_5H_5) ppm. ^{13}C NMR (75 MHz, CDCl_3): $\delta = 189.0$ ($\text{C}=\text{O}$), 98 (C_5H_5) ppm. IR (CH_2Cl_2): $\tilde{\nu} = 2207$ [$\text{v}(\text{C}\equiv\text{C})$], 1524 [$\text{v}(\text{C}=\text{O})$] cm^{-1} . FAB-MS: $m/z = 897.1$ [P^+], 690.9 [$\text{P} - \text{dpp}$] $^+$, 634.8 [$\text{P} - \text{PPh}_3$] $^+$. $\text{C}_{56}\text{H}_{45}\text{OF}_6\text{P}_3\text{Ru}$ (1041.95): C 64.55, H 4.35; found C 64.44, H 4.27.

IR Spectroscopic Monitoring of the Reaction of [CpRu(PPh₃)₂][PF₆ with 1,3-Diphenylpropynone: Under an atmosphere of dry argon, [CpRu(PPh₃)₂Cl] (0.40 g, 0.96 mmol) was mixed with AgPF₆ (0.24 g, 0.96 mmol) in CH₂Cl₂ (50 mL). The solution was stirred for 30 min, and a portion (7.0 mL) of the mixture was then transferred by syringe into a cell equipped with a fiber optic FTIR probe. Two spectra were recorded that showed a flat baseline and a peak at 2181 cm⁻¹ [ν(N≡N)] and then 1,3-diphenylpropynone (0.14 g, 0.67 mmol) was added. Thirty spectra were recorded over 20 min: the spectra contained peaks at 2197 and 1532 cm⁻¹ that decreased in intensity and at 1658, 1596, 1580, and 1558 cm⁻¹ that increased in intensity; a strong peak at 1641 cm⁻¹ decreased slightly in intensity; and an isosbestic point at 1528 cm⁻¹. These spectra are plotted in Figure S2 (Supporting Information). A KBr-pellet IR spectrum of 2Bar^F₄ is plotted in Figure S3.

Supporting Information (see footnote on the first page of this article): Experimental procedures and characterization data for the three vinylidene cations 2Bar^F₄, crystal structure of 2Bar^F₄, and IR spectra.

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- [11] Single crystals were grown by cooling a saturated Et₂O solution to –30 °C. Data for 2aBar^F₄ at 100 K: C₈₈H₅₇BF₂₄OP₂Ru 1760.16 g mol⁻¹, triclinic, space group *P* $\bar{1}$, *a* = 12.3691(8) Å, *b* = 17.6970(10) Å, *c* = 18.1997(11) Å, *a* = 104.163(3)°, *β* = 92.766(4)°, *γ* = 99.179(3)°, *V* = 3797.4(4) Å³, *Z* = 2, *D*_{calcd.} = 1.539 Mg m⁻³, *R*₁ = 0.0656 for 12197 reflections with *I* > 2σ(*I*), *wR*₂ = 0.1199 for 17959 reflections (*R*_{int} = 0.074, with a measured total number of 64083 reflections), GOF on *F*² = 1.024, largest diff. peak (hole) = 1.046 (–0.830) e Å⁻³. CCDC-647871 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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