

Structural Characterization of Alkyne and Vinylidene Isomers of $[\text{Ru}(\text{C}_2\text{H}_2)(\text{PMe}_2\text{Ph})_2(\text{Cp})][\text{BF}_4]$

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Abstract: The reaction of $[\text{RuCl}(\text{PMe}_2\text{Ph})_2(\text{Cp})]$ with ethyne and TIBF_4 in dichloromethane leads to $[\text{Ru}(\eta^2\text{-HC}\equiv\text{CH})(\text{PMe}_2\text{Ph})_2(\text{Cp})][\text{BF}_4]$ (**2**), an unusual η^2 -alkyne complex of a d^6 metal center. This ethyne complex smoothly rearranges to its vinylidene isomer, $[\text{Ru}(\text{C}=\text{CH}_2)(\text{PMe}_2\text{Ph})_2(\text{Cp})][\text{BF}_4]$ (**4**), above ca. 60 °C in acetone solution. The η^2 -ethyne to vinylidene conversion can also be carried out by deprotonation of **2** to give $[\text{Ru}(\text{C}\equiv\text{CH})(\text{PMe}_2\text{Ph})_2(\text{Cp})]$ (**3**), followed by protonation of **3** to give exclusively vinylidene isomer **4**. Structures of both **2** and **4** were determined by X-ray diffraction. Aside from the difference in the geometry of the C_2H_2 ligands, the structures are nearly identical. Crystal data with $\text{Mo K}\alpha$ ($\lambda = 0.7107$ Å) radiation at 297 K are as follows: **2**, $\text{C}_{23}\text{H}_{29}\text{BF}_4\text{P}_2\text{Ru}$, $a = 23.099$ (3) Å, $b = 9.203$ (2) Å, $c = 11.344$ (3) Å, orthorhombic space group $Pca2_1$ (No. 29), $Z = 4$, $R = 0.054$, $R_w = 0.074$; **4**, $\text{C}_{23}\text{H}_{29}\text{BF}_4\text{P}_2\text{Ru}$, $a = 23.270$ (3) Å, $b = 9.290$ (1) Å, $c = 11.3659$ (8) Å, orthorhombic space group $Pca2_1$ (No. 29), $Z = 4$, $R = 0.035$, $R_w = 0.044$.

Introduction

The ethyne to vinylidene ($\text{C}\equiv\text{CH}_2$) rearrangement is a fundamentally important transformation which is strongly endothermic in the gas phase. This rearrangement has an experimental activation barrier of 155 (8) kJ mol⁻¹ as studied by modulated beam dynamic mass spectrometry.¹ The $^1\text{A}_1$, $^3\text{B}_2$, and $^3\text{A}_2$ states of vinylidene are calculated to lie about 188, 364, and 389 kJ mol⁻¹ above ethyne,²⁻⁷ respectively, with vinylidene to ethyne activation barriers between 4 and 26 kJ mol⁻¹.^{4,6,7} (These values strongly depend upon the computational method.) Lineberger and co-workers have observed singlet and triplet vinylidenes in ultraviolet photoelectron spectra of vinylidene anions.⁸⁻¹⁰ On certain metal surfaces and metal complexes, ethyne spontaneously converts to vinylidene.^{11,12} For example, reactions of $[\text{M}(\text{PR}_3)_2(\text{Cp})]^+$ ($\text{M} = \text{Fe, Ru, Os}$) sources with 1-alkynes normally lead to vinylidene complexes $[\text{M}(\text{C}=\text{CRH})(\text{PR}_3)_2(\text{Cp})]^+$ without observed $[\text{M}(\eta^2\text{-RC}\equiv\text{CH})(\text{PR}_3)_2(\text{Cp})]^+$ intermediates.¹³⁻¹⁵ However, Bullock recently reported the room-temperature isolation of $[\text{Ru}(\eta^2\text{-HC}\equiv\text{CH})(\text{PMe}_2\text{Ph})_2(\text{Cp})][\text{BF}_4]$, which gradually rearranges to $[\text{Ru}(\text{C}=\text{CH}_2)(\text{PMe}_2\text{Ph})_2(\text{Cp})][\text{BF}_4]$ at about 60 °C.¹⁶ In a parallel study, we isolated similar metastable η^2 -ethyne complexes of other sterically nondemanding $[\text{M}(\text{PR}_3)_2(\text{Cp})]^+$ metal centers ($\text{M} = \text{Fe, Ru}$; $\text{PR}_3 = \text{P}(\text{OMe})_3, \text{PMe}_3, \text{PMe}_2\text{Ph}, 1/2 \text{ } o\text{-}(\text{PMe}_2)_2\text{C}_6\text{H}_4, 1/2 \text{ Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$).¹⁷ A comprehensive study of the rearrangement of these compounds to their more stable vinylidene forms will be reported separately. Here, we report the preparation

and structural characterization of both alkyne and vinylidene forms of $[\text{Ru}(\text{C}_2\text{H}_2)(\text{PMe}_2\text{Ph})_2(\text{Cp})][\text{BF}_4]$, the first structurally characterized pair of C_2H_2 isomers.

Experimental Section

Unless otherwise noted, all preparations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. All solvents were dried using appropriate drying agents, freshly distilled, and collected under nitrogen before use. $[\text{RuCl}(\text{PPh}_3)_2(\text{Cp})]$ was prepared according to Bruce.¹⁸ TIBF_4 was prepared from Ti_2CO_3 and aqueous HBF_4 . Ethyne (Air Products), $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (Aldrich), PMe_2Ph (Aldrich), and KOCMe_3 (Strem) were obtained commercially. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrophotometer, and ^{31}P NMR spectra on either a Varian VXR-400 (162 MHz) or a Varian XL-200 (81 MHz). ^1H and ^{13}C NMR spectra were referenced to the solvent peak; ^{31}P NMR spectra were referenced to external H_3PO_4 . IR data were recorded on a Perkin-Elmer 1710 FTIR spectrometer. Analyses were performed by Canadian Microanalytical Service Ltd. (Delta, BC).

Preparation of $[\text{RuCl}(\text{PMe}_2\text{Ph})_2(\text{Cp})]$ (1**).** Using a modified literature procedure,¹⁹ $[\text{RuCl}(\text{PPh}_3)_2(\text{Cp})]$ (5.00 g, 6.89 mmol), PMe_2Ph (2.35 mL, 16.5 mmol), and toluene (60 mL) were heated to reflux for 5 h. The warm solution was cannulated onto a 2×20 cm alumina column (Brockman activity 11). Elution with hexane (500 mL) removed PPh_3 and excess PMe_2Ph . The product was eluted as a yellow band with 50/50 hexane/chloroform. The solvent was removed on a rotary evaporator to give a dark orange oil, which was triturated with pentane for 2 h and then dried in vacuo to give 2.32 g (70%) of **1** as an orange solid. NMR data are identical to reported values.

Preparation of $[\text{Ru}(\eta^2\text{-C}_2\text{H}_2)(\text{PMe}_2\text{Ph})_2(\text{Cp})][\text{BF}_4]$ (2**).** $[\text{RuCl}(\text{PMe}_2\text{Ph})_2(\text{Cp})]$ (1.50 g, 3.14 mmol) and TIBF_4 (1.12 g, 3.84 mmol) were dissolved in CH_2Cl_2 (30 mL) in a 100-mL Schlenk flask sealed with a rubber septum. Ethyne, passed through concentrated H_2SO_4 , soda lime, and granular CaSO_4 , was bubbled through the solution for 5 min. The flask was sealed under ethyne pressure, and the solution was stirred vigorously overnight. The resulting yellow solution was filtered to remove TiCl_4 and unreacted TIBF_4 and evaporated to 5 mL in vacuo. Ethyl ether (50 mL) was slowly added to precipitate 1.43 g (82%) of **2** as a yellow-tan powder: mp 150 °C dec; ^1H NMR (200 MHz, $(\text{CD}_3)_2\text{CO}$) δ_{H} 7.48 (m, 10 H, Ph), 5.57 (t, $^3J_{\text{PH}} = 6.7$ Hz, 2 H, HCCH), 5.27 (s, 5 H, Cp), 1.79 (vt, $^2J_{\text{PH}} + ^4J_{\text{PH}} = 9.5$ Hz, 6 H, Me), 1.51 (vt, $^2J_{\text{PH}} + ^4J_{\text{PH}} = 9.4$ Hz, 6 H, Me'); $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, $(\text{CD}_3)_2\text{CO}$) δ_{C} 139.8 (t, $^1J_{\text{PC}} = 24.3$ Hz, ipso-Ph), 130.7 (s, Ph), 130.5 (t, Ph), 129.1 (t, Ph), 87.6 (s, Cp), 60.4 (br s, C=C), 20.0 (vt, $^1J_{\text{PC}} + ^3J_{\text{PC}} = 35.4$ Hz, Me), 15.9 (vt, $^1J_{\text{PC}} + ^3J_{\text{PC}} = 35.9$ Hz, Me'); ^{13}C NMR (50 MHz, $(\text{CD}_3)_2\text{CO}$, gated decoupling) δ_{C} 87.6 ($^1J_{\text{CH}} = 180.6$ Hz, $^2J_{\text{CH}} = 6.8$ Hz, $^3J_{\text{CH}} = 1.6$ Hz, Cp), 60.4 ($^1J_{\text{CH}} = 245.4$ Hz, $^2J_{\text{CH}} = 34.5$ Hz, $^3J_{\text{PC}} = 3.2$ Hz, C=C), 20.0 ($^1J_{\text{CH}} = 130.9$ Hz, Me), 15.9 ($^1J_{\text{CH}} = 130.7$ Hz, Me'); ^{31}P NMR (162 MHz, $(\text{CD}_3)_2\text{CO}$) δ_{P} 18.4 (s); IR (CH_2Cl_2 , cm^{-1}) 3944 (s), 3055 (vs),

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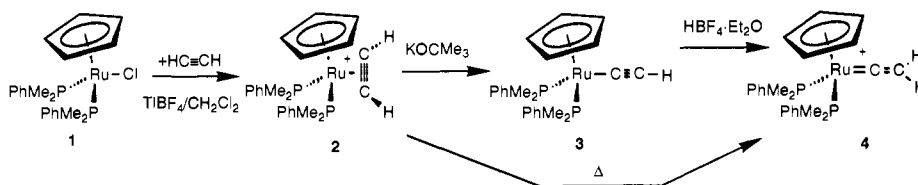
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Scheme 1



2987 (vs), 2686 (s), 2411 (w), 2359 (w), 2306 (s), 1750 (w, C≡C), 1422 (vs), 1258 (vs), 1060 (vs, BF₄), 940 (w), 897 (vs), 764 (vs). Anal. Calcd for C₂₃H₂₉P₂RuBF₄: C, 49.75; H, 5.26. Found: C, 49.80; H, 5.41.

Preparation of [Ru(C≡CH)(PMe₂Ph)₂(Cp)] (3). [Ru(η²-C₂H₂)(PMe₂Ph)₂(Cp)] [BF₄] (1.43 g, 2.57 mmol) and KOCMe₃ (0.346 g, 3.08 mmol) were stirred in ethyl ether (40 mL) under argon. The resulting yellow solution was filtered and evaporated to dryness in vacuo. A minimum of pentane was added to dissolve the yellow solid. The solution was cooled to -40 °C overnight. Long yellow needle crystals of 3 (0.948 g, 79% yield) were isolated by decanting the supernatant pentane using a cannula and drying in vacuo: mp 102–104 °C; ¹H NMR (200 MHz, C₆D₆) δ_H 7.52 (m, 4 H, *o*-Ph), 7.11 (m, 6 H, *m*-, *p*-Ph), 4.47 (s, 5 H, Cp), 2.21 (t, ⁴J_{PH} = 2.6 Hz, 1 H, C≡CH), 1.56 (vt, ²J_{PH} + ⁴J_{PH} = 9.4 Hz, 6 H, Me), 1.51 (vt, ²J_{PH} + ⁴J_{PH} = 9.1 Hz, 6 H, Me); ¹³C{¹H} NMR (50 MHz, C₆D₆) δ_C 145.2 (vt, ¹J_{PC} + ³J_{PC} = 40.2 Hz, *ipso*-Ph), 130.8 (t, Ph), 128.4 (m, Ph), 108.7 (t, ²J_{PC} = 25.0 Hz, C_α), 93.3 (s, C_β), 82.6 (s, Cp), 22.1 (vt, ¹J_{PC} + ³J_{PC} = 31.6 Hz, Me), 19.3 (vt, ¹J_{PC} + ³J_{PC} = 30.9 Hz, Me); ³¹P NMR (162 MHz, C₆D₆) δ_P 22.9 (s); IR (CH₂Cl₂, cm⁻¹) 3271 (s, C≡CH), 3054 (s), 2976 (s), 2911 (s), 2306 (w), 1925 (vs, C≡C), 1435 (vs), 1274 (vs), 1258 (vs), 1098 (s), 992 (w), 903 (vs). Anal. Calcd for C₂₃H₂₈P₂Ru: C, 59.09; H, 6.04. Found: C, 58.87; H, 5.94.

Preparation of [Ru(C≡CH₂)(PMe₂Ph)₂(Cp)] [BF₄] (4). HBF₄·Et₂O (0.025 g, 0.153 mmol) was added to a solution of [Ru(C≡CH)(PMe₂Ph)₂(Cp)] (0.074 g, 0.158 mmol) in CH₂Cl₂ (30 mL) under argon. The resulting yellow-red solution was stirred for 5 min before reducing the volume to 5 mL in vacuo. Ethyl ether (50 mL) was slowly added to precipitate the product as a mustard-yellow powder. After removal of the supernatant, the solid was washed with three 30-mL portions of ethyl ether and dried in vacuo to give 4 (0.58 g, 68%): mp 150 °C dec; ¹H NMR (200 MHz, (CD₃)₂CO) δ_H 7.53 (m, 10 H, Ph), 5.53 (s, 5 H, Cp), 4.30 (t, ⁴J_{PH} = 2.2 Hz, 2 H, CH₂), 1.84 (vt, ²J_{PH} + ⁴J_{PH} = 10.2 Hz, 6 H, Me), 1.76 (vt, ²J_{PH} + ⁴J_{PH} = 10.2 Hz, 6 H, Me); ¹³C{¹H} NMR (50 MHz, (CD₃)₂CO) δ_C 346.2 (t, ²J_{PC} = 15.7 Hz, C_α), 139.2 (vt, ¹J_{PC} + ³J_{PC} = 52.4 Hz, *ipso*-Ph), 130.7 (s, Ph), 130.3 (t, Ph), 129.1 (t, Ph), 93.8 (s, C_β), 92.2 (s, Cp), 19.6 (vt, ¹J_{PC} + ³J_{PC} = 36.8 Hz, Me), 18.3 (vt, ¹J_{PC} + ³J_{PC} = 37.7 Hz, Me); ³¹P NMR (81 MHz, (CD₃)₂CO) δ_P 18.3 (s); IR (Nujol, cm⁻¹) 2950 (vs), 2940 (vs), 2850 (vs), 2385 (w), 1650 (s, C=C), 1470 (vs), 1275 (w), 1060 (vs, BF₄), 925 (w), 800 (w), 730 (w). Anal. Calcd for C₂₃H₂₉P₂RuBF₄: C, 49.75; H, 5.26. Found: C, 49.60; H, 5.28.

Crystal Structure Determinations of 2 and 4. Crystal structure calculations were performed on an IBM 3090 computer system, using the direct methods difference Fourier program DIRDIF,²⁰ local version of Ibers' NUCLS least-squares program (based on the Busing-Levy ORFLS), Zalkin's FORDAP Fourier program, the Busing-Levy ORFFE error function program, and Johnson's ORTEP thermal ellipsoid plotting program. Anomalous dispersion corrections were included for the scattering of Ru, P, and F atoms.

Crystals of 2 and 4 suitable for X-ray diffraction were obtained by slow diffusion of ethyl ether vapor into concentrated CH₂Cl₂ solutions of the compounds at room temperature. The crystals were coated with epoxy and mounted on glass fibers, nearly aligned along the long axes of the crystals. Crystal properties and details of X-ray data collection, solution, and refinement are listed in Table 1.

For both 2 and 4, the ruthenium atom was located by using the Patterson function in DIRDIF. The phosphorus atoms were located by using DIRDIF, and the remaining non-hydrogen atoms by using difference Fourier methods. Structure 2 was initially solved in the centrosymmetric space group *Pbcm* (No. 57), but was transformed and refined in the noncentrosymmetric space group *Pca2*₁ (No. 29). At least one hydrogen atom was located on each methyl group; the remaining methyl, phenyl and cyclopentadienyl hydrogen atoms were placed in calculated positions. Hydrogen atoms were not located on the ethyne nor vinylidene ligands, and no attempt was made to place them artificially. Isotropic thermal parameters for hydrogen atoms were equal to *B*(attached carbon) + 1.0;

Table I. Crystallographic Data and Experimental Details for [Ru(η²-HC≡CH)(PMe₂Ph)₂(Cp)] [BF₄] (2) and [Ru(C≡CH₂)(PMe₂Ph)₂(Cp)] [BF₄] (4)

	compd 2	compd 4
formula	C ₂₃ H ₂₉ BF ₄ P ₂ Ru	C ₂₃ H ₂₉ BF ₄ P ₂ Ru
form weight	555.306 amu	555.306 amu
color and form	yellow block	yellow block
space group	<i>Pca2</i> ₁ (No. 29)	<i>Pca2</i> ₁ (No. 29)
<i>a</i> , Å	23.099 (3)	23.270 (3)
<i>b</i> , Å	9.203 (2)	9.290 (1)
<i>c</i> , Å	11.344 (3)	11.3659 (8)
vol Å ³	2411.6 (8)	2457.1 (4)
temp, K	297 (1)	297 (1)
<i>Z</i>	4	4
imposed symmetry	none	none
density (calcd), g cm ⁻³	1.529	1.501
<i>F</i> (000), e	1128	1128
<i>F</i> (000) corrected e	1123.3	1123.3
cryst dimensions, mm ³	0.60 × 0.45 × 0.25	0.50 × 0.45 × 0.25
abs coeff μ (Mo Kα), cm ⁻¹	8.059	7.910
diffractometer	Enraf-Nonius CAD-4	Enraf-Nonius CAD-4
radiation	Mo Kα (λ = 0.7107 Å)	Mo Kα (λ = 0.7107 Å)
monochromator	graphite	graphite
2θ range	2–25°	2–25°
scan type	ω–2θ	ω–2θ
scan range	0.75° + 0.35° tan θ	0.60° + 0.35° tan θ
max counting time, s	90	90
<i>h</i> range	0–27	–27–0
<i>k</i> range	–10–0	0–11
<i>l</i> range	–13–0	–13–0
X-ray exposure, h	43.8	42.5
no. of std refls	3	3
max variation std refls	8% (random)	7% (random)
absorption correction	none	none
total data collected	2236	2502
unique data collected	2236	2502
data with <i>I</i> > 3σ(<i>I</i>)	1961	1942
no. of variables	245	256
<i>R</i> ^a	0.054	0.035
<i>R</i> _w ^a	0.074	0.044
GOF ^b	4.4104	2.5438
(Δ/σ) _{max}	0.89 (z of F4)	0.32 (β ₂₃ of C4)
Δρ _{max}	0.088 e Å ⁻³	0.053 e Å ⁻³
	near Cp5	near BF ₄ ⁻

^a $R = (\sum ||F_o| - |F_c|| / \sum |F_o|)$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$, where $w = 4I / (\sigma^2(I) + 0.02I^2)$. ^b GOF = $[\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$.

positions and *B* values were adjusted after each set of least-squares cycles. For compound 2, the cyclopentadienyl ligand would not refine as five independent carbon atoms, so it was refined as a rigid group with independent isotropic thermal parameters on each carbon atom. For 4, the disordered BF₄⁻ anion was modeled as two overlapping, rigid BF₄⁻ groups, each at 50% occupancy, with independent isotropic thermal parameters on each atom. Other non-hydrogen atoms were refined with anisotropic thermal parameters. No corrections for decay, extinction, or absorption were applied to the data.

Results

Synthesis. The reaction of [RuCl(PMe₂Ph)₂(Cp)] (1) with ethyne is carried out in dichloromethane by using TIBF₄ as a chloride abstractor (Scheme I). Simple filtration to remove insoluble TiCl₄ and unreacted TIBF₄, followed by precipitation with ethyl ether gives exclusively yellow [Ru(η²-C₂H₂)(PMe₂Ph)₂(Cp)] [BF₄] (2) in 82% yield. This η² form is stable indefinitely

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Table II. Selected Bond Distances (Å) with esd's for the Structures of $[\text{Ru}(\eta^2\text{-HC}\equiv\text{CH})(\text{PMe}_2\text{Ph})_2(\text{Cp})][\text{BF}_4]$ (**2**) and $[\text{Ru}(\text{C}=\text{CH}_2)(\text{PMe}_2\text{Ph})_2(\text{Cp})][\text{BF}_4]$ (**4**)

		2	4
Ru	P1	2.317 (3)	2.313 (2)
Ru	P2	2.304 (3)	2.308 (2)
Ru	Cp0 ^a	1.882	1.902
Ru	Mp ^b	2.124	
Ru	C1	2.204 (18)	1.843 (10)
Ru	C2	2.209 (16)	
P1	C3	1.819 (13)	1.803 (8)
P1	C4	1.791 (14)	1.826 (8)
P1	C5	1.810 (14)	1.814 (8)
P2	C11	1.836 (13)	1.822 (8)
P2	C12	1.804 (14)	1.806 (9)
P2	C13	1.826 (12)	1.820 (8)
C1	C2	1.224 (21)	1.287 (13)

^aCp0 is the centroid of the Cp1–Cp5 cyclopentadienyl ring. ^bMp is the midpoint of the C1–C2 bond.

Table III. Selected Bond Angles (deg) with esd's for the Structures of $[\text{Ru}(\eta^2\text{-HC}\equiv\text{CH})(\text{PMe}_2\text{Ph})_2(\text{Cp})][\text{BF}_4]$ (**2**) and $[\text{Ru}(\text{C}=\text{CH}_2)(\text{PMe}_2\text{Ph})_2(\text{Cp})][\text{BF}_4]$ (**4**)

				2	4
Cp0	Ru	Mp		121.0	
Cp0	Ru	C1		122.0	122.9
Cp0	Ru	C2		117.4	
Cp0	Ru	P2		126.6	126.4
Cp0	Ru	P1		120.9	121.8
Mp	Ru	P2		90.6	
Mp	Ru	P1		98.2	
C1	Ru	C2		32.2 (5)	
C1	Ru	P2		100.1 (5)	90.9 (3)
C1	Ru	P1		85.0 (5)	92.7 (3)
C2	Ru	P2		80.9 (4)	
C2	Ru	P1		111.1 (5)	
P2	Ru	P1		91.6 (1)	92.8 (1)
C4	P1	C5		100.2 (6)	102.0 (4)
C4	P1	C3		101.1 (6)	102.8 (4)
C4	P1	Ru		114.6 (5)	111.3 (3)
C5	P1	C3		102.5 (6)	104.0 (4)
C5	P1	Ru		122.0 (4)	120.0 (2)
C3	P1	Ru		113.6 (4)	114.7 (3)
C12	P2	C13		101.6 (6)	102.1 (4)
C12	P2	C11		99.0 (7)	101.5 (4)
C12	P2	Ru		114.2 (5)	112.4 (3)
C13	P2	C11		104.0 (6)	104.9 (4)
C13	P2	Ru		118.2 (4)	117.6 (2)
C11	P2	Ru		117.1 (5)	116.2 (3)
C2	C1	Ru		74.1 (12)	174.1 (8)
C1	C2	Ru		73.7 (11)	

^aCp0 is the centroid of the Cp1–Cp5 cyclopentadienyl ring. ^bMp is the midpoint of the C1–C2 bond.

in the solid phase at room temperature. Rearrangement to $[\text{Ru}(\text{C}=\text{CH}_2)(\text{PMe}_2\text{Ph})_2(\text{Cp})][\text{BF}_4]$ (**4**) occurs very slowly in solution at temperatures below about 50 °C. The half-life for rearrangement to **4** is 18 min at 65 °C. Details of the rearrangement of **2** and related compounds will be reported separately.

$[\text{Ru}(\text{C}=\text{CH}_2)(\text{PMe}_2\text{Ph})_2(\text{Cp})][\text{BF}_4]$ (**4**) can be isolated from the rearrangement of **2**, but it is more conveniently prepared by the stepwise deprotonation and protonation of **2**. The deprotonation of **2** with potassium *tert*-butoxide gives the ethynyl complex $[\text{Ru}(\text{C}\equiv\text{CH})(\text{PMe}_2\text{Ph})_2(\text{Cp})]$ (**3**) nearly quantitatively, although its high solubility in pentane allows its isolation in only 79% yield. Protonation of **3** with a tetrafluoroboric acid–ethyl ether complex in dichloromethane gives exclusively vinylidene isomer $[\text{Ru}(\text{C}=\text{CH}_2)(\text{PMe}_2\text{Ph})_2(\text{Cp})][\text{BF}_4]$ (**4**) in 68% isolated yield.

Structures. Crystal structures of both the η^2 -alkyne (**2**) and vinylidene (**4**) isomers of $[\text{Ru}(\text{C}_2\text{H}_2)(\text{PMe}_2\text{Ph})_2(\text{Cp})][\text{BF}_4]$ were determined by X-ray diffraction. Selected bond distances and bond angles are listed in Tables II and III. ORTEP plots are shown in Figures 1–3. The structures are very similar, differing significantly only in the bonding mode of the C_2H_2 ligand. In **2**, the η^2 -ethyne ligand is symmetrically bound to Ru, with Ru–C dis-

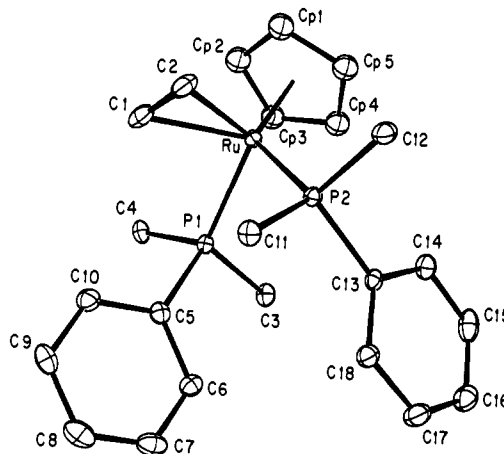


Figure 1. Perspective drawing of the molecular structure of the cation of $[\text{Ru}(\eta^2\text{-HC}\equiv\text{CH})(\text{PMe}_2\text{Ph})_2(\text{Cp})][\text{BF}_4]$ (**2**). The ellipsoids correspond to 50% probability contours of atomic displacement. The hydrogen atoms have been omitted for the sake of clarity.

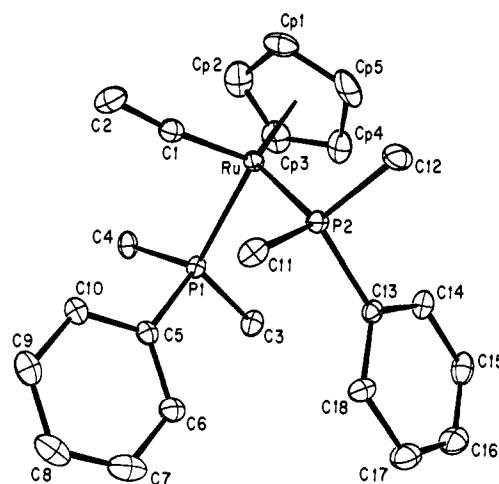


Figure 2. Perspective drawing of the molecular structure of the cation of $[\text{Ru}(\text{C}=\text{CH}_2)(\text{PMe}_2\text{Ph})_2(\text{Cp})][\text{BF}_4]$ (**4**).

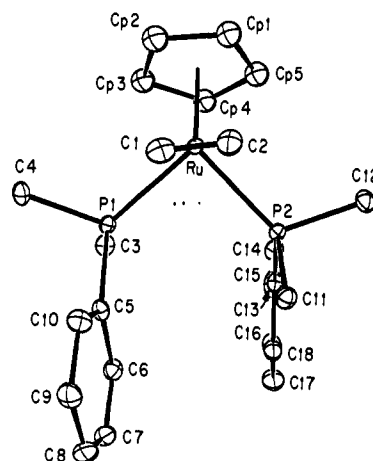


Figure 3. Perspective drawing of the molecular structure of $[\text{Ru}(\eta^2\text{-HC}\equiv\text{CH})(\text{PMe}_2\text{Ph})_2(\text{Cp})]^+$ (**3**) projected along the Ru–alkyne bond.

tances of 2.20 (2) and 2.21 (2) Å and a C1–C2 distance of 1.22 (2) Å. The vinylidene ligand in **4** is bound to Ru with an Ru–C distance of 1.84 (1) Å, a C1–C2 distance of 1.29 (1) Å, and an Ru–C1–C2 angle of 174.1 (8)°. The η^2 -ethyne ligand in **2** occupies slightly more space on the coordination sphere, resulting in a slightly smaller P1–Ru–P2 angle in **2** (91.6 (1)°) than in **4** (92.8 (1)°). In both structures, one PMe_2Ph phenyl group is directed toward the alkyne or vinylidene ligand, and the other PMe_2Ph

Table IV. NMR Properties of Selected Mononuclear Transition Metal η^2 -Ethyne Complexes

complex	δ_{H} (HC \equiv CH)	δ_{C} (HC \equiv CH)	$^1J_{\text{CH}}$ (Hz)	$^2J_{\text{CH}}$ (Hz)	$^3J_{\text{PH}}$ (Hz)	$^2J_{\text{PC}}$ (Hz)
Four-Electron η^2 -Ethyne Complexes						
[Mo(η^2 -HC \equiv CH)(Me ₃ CN \equiv C) ₂ (SCMe ₃) ₂] ^{28,29}	10.43	171.7	215			
[Mo(η^2 -HC \equiv CH)(CO)(PPh ₃)(Cp)][BF ₄] ³⁰	12.03, 12.86					
[W(η^2 -HC \equiv CH)(CO)(S ₂ CNET ₂) ₂] ^{25,31}	12.5, 13.5	206, 207	210, 210			
[W(η^2 -HC \equiv CH)Cl ₄ (Et ₂ O)] ³²	17.5	215.5	233.8			
Two-Electron η^2 -Ethyne Complexes						
[Re(η^2 -HC \equiv CH)(NO)(PPh ₃)(Cp)][BF ₄] ^{23,24}	6.72, 8.63	84.5, 89.7	242.1, 237.7	23.6, 23.5	18.7, 4.7	14.1
[Re(η^2 -HC \equiv CH)(CO) ₂ (Cp)] ³³	5.61	64.5	237	27.3		
[Ru(η^2 -HC \equiv CH)(PMe ₃) ₂ (Cp)][BF ₄] ¹⁶	4.98	62.4				
[Ru(η^2 -HC \equiv CH)(PMe ₂ Ph) ₂ (Cp)][BF ₄]	5.57	60.4	245.4	34.5	6.7	3.2
[Ni(η^2 -HC \equiv CH)(PPh ₃) ₂] ³⁴	6.41	122.1	212	32.8 ^a		8.7
[Cu(η^2 -HC \equiv CH){HN(2-C ₅ H ₄ N) ₂ }] [BF ₄] ^{35,36}	5.59					

^a Assigned as $^3J_{\text{PC}}$ by Pörschke et al.; reassigned here for consistency with other data.

phenyl group is directed away from the alkyne or vinylidene ligand. The relevant torsion angles are Mp–Ru–P1–C5 = –46.7° and Mp–Ru–P2–C13 = 151.6° for **2** (Mp is the midpoint of the C1–C2 vector), and C1–Ru–P1–C5 = –46.1° and C1–Ru–P2–C13 = 145.3° for **4**.

Discussion

Synthesis. The synthesis of [Ru(η^2 -C₂H₂)(PMe₂Ph)₂(Cp)][BF₄] (**2**) by using TlBF₄ in CH₂Cl₂ is straightforward. We find this method generally useful for the preparation of [Ru(L)(PR₃)₂(Cp)]⁺ complexes from halide precursors, because it avoids the expense, oxidizing ability, and hygroscopic behavior of AgBF₄, and it eliminates side reactions from often-used reactive solvents such as methanol and acetonitrile. Bullock prepared [Ru(η^2 -HC \equiv CH)(PMe₃)₂(Cp)][PF₆] from the chloride by using ethyne and NH₄PF₆ in methanol.¹⁶ This method works for the PMe₂Ph compound, but reproducibility and yields are higher using TlBF₄. [Ru(η^2 -HC \equiv CH)(PMe₂Ph)₂(Cp)][BF₄] (**2**) is the kinetic product of the reaction of "[Ru(PMe₂Ph)₂(Cp)]⁺" with ethyne. With the exception of [Ru(η^2 -HC \equiv CR)(PMe₃)₂(Cp)][BF₄] (R = H, Me) reported by Bullock, all other d⁶ [M(η^2 -HC \equiv CR)L₂(Cp)]⁺ complexes rearrange rapidly to their thermodynamically favored vinylidene isomers or undergo other secondary reactions.^{14,15} In these cases, the η^2 -HC \equiv CR form is destabilized by the unfavorable overlap of filled metal d_z orbitals with the filled π_{\perp} orbitals of the coordinated alkyne, whereas the vinylidene form is favored by π -donation from the metal to the low-lying vinylidene π^* orbital.^{11,12,21,22} In the case of **2** and Bullock's complexes, it appears that isolation of the kinetic η^2 -alkyne products is made possible by small alkyne substituents and small ancillary ligands on ruthenium. In our PMe₂Ph system, propyne gives a mixture of [Ru(η^2 -HC \equiv CMe)(PMe₂Ph)₂(Cp)][BF₄] and [Ru(C=CMeH)(PMe₂Ph)₂(Cp)][BF₄] at room temperature. With larger ancillary ligands PPh₃, Ph₂PCH₂PPh₂, and Ph₂PCH₂CH₂PPh₂, even η^2 -ethyne complexes are not isolated.

Gładysz and co-workers have obtained alkyne complexes [Re(η^2 -HC \equiv CR)(NO)(PPh₃)(Cp)][BF₄] (R = H, CMe₃) from labile [Re(ClC₆H₅)(NO)(PPh₃)(Cp)][BF₄] and HC \equiv CR.^{23,24} The η^2 -ethyne complex does not convert to known [Re(C=C₂H₂)(NO)(PPh₃)(Cp)][BF₄] after 2 h in C₆D₅Cl at 90 °C. The η^2 -3,3-dimethyl-1-butyne (*tert*-butylacetylene) complex converts into a mixture (74/12/14) of the two geometric isomers of the vinylidene complex [Re(C=CHCMe₃)(NO)(PPh₃)(Cp)][BF₄] and unconverted alkyne complex over the course of 1 h in C₆D₅Cl at 80 °C. A similar mixture is obtained starting with [Re(C=CHCMe₃)(NO)(PPh₃)(Cp)][BF₄] at 80 °C for 2 h, demonstrating the establishment of a true thermal equilibrium in the rhenium system. In contrast, we have never obtained the η^2 form of any alkyne larger than propyne nor observed the conversion of a vinylidene complex back to its η^2 -alkyne isomer in the ruthenium

system. These differences probably arise from the larger size and more inert character of Re(I) compared to Ru(II).

Spectroscopy. Spectroscopic properties of the η^2 -ethyne and vinylidene isomers **2** and **4** are distinctly different. The NMR spectra of [Ru(η^2 -C₂H₂)(PMe₂Ph)₂(Cp)][BF₄] (**2**) display phosphorus-coupled triplets for the ethyne hydrogens (δ_{H} 5.57, $^3J_{\text{PH}}$ = 6.7 Hz) and carbons (δ_{C} 60.4, $^2J_{\text{PC}}$ = 3.2 Hz). The ethyne carbon–hydrogen coupling constants are $^1J_{\text{CH}}$ = 245.4 Hz and $^2J_{\text{CH}}$ = 34.5 Hz. Spectroscopic data for several η^2 -ethyne complexes are collected in Table IV. The ¹H and ¹³C shifts of alkyne ligands correlate well with the number of electrons donated to the metal (or electron deficiency at the metal).^{22,25} δ_{H} is 5–7 for most two-electron alkynes (except [Re(η^2 -HC \equiv CH)(NO)(PPh₃)(Cp)][BF₄],²³ Table IV) and 9–18 for four-electron alkynes; δ_{C} is about 60–120 for two-electron alkynes and 175–240 for four-electron alkynes. The two-electron ethyne ligand of complex **2** displays a typical ¹H NMR signal but a ¹³C signal at the high-field end of the range. The large $^1J_{\text{CH}}$ of **2** is almost the same as that of free ethyne (249 Hz), suggesting very little rehybridization at carbon upon coordination to ruthenium.^{23,26,27}

The vinylidene ligand in [Ru(C=C₂H₂)(PMe₂Ph)₂(Cp)][BF₄] (**4**) displays a vinylic ¹H NMR triplet (δ_{H} 4.30, $^4J_{\text{PH}}$ = 2.2 Hz), a highly deshielded C _{α} triplet (δ_{C} 346.2, $^2J_{\text{PC}}$ = 15.7 Hz), and a vinylic C _{β} singlet (δ_{C} 93.8), which is typical of phosphine-substituted ethynylidene complexes.^{14,15,17,23,24} ³¹P NMR shifts of the dimethylphenylphosphine ligands are virtually unaffected by the isomerization of the C₂H₂ ligand (δ_{P} 18.4 for **2**, 18.3 for **4**). In the infrared spectra, a weak coordinated C \equiv C stretch absorbing at 1750 cm⁻¹ in **2** is replaced by a strong vinylidene C=C stretch at 1650 cm⁻¹ in **4**.

The NMR spectra of [Ru(C=C₂H₂)(PMe₂Ph)₂(Cp)] (**3**) display a phosphorus-coupled triplet for the ethyne hydrogens (δ_{H} 2.21, $^4J_{\text{PH}}$ = 2.6 Hz) and a triplet and singlet for the ethynyl carbons (δ_{C} (C _{α}) 108.7, $^2J_{\text{PC}}$ = 25.0 Hz; δ_{C} (C _{β}) 93.3). Infrared absorptions occur at 3271 and 1925 cm⁻¹ for the ethynyl C–H and C \equiv C stretching modes. Electron-rich metal ethynyls typically show C \equiv C stretching frequencies about 100 cm⁻¹ lower than substituted metal alkynyls.

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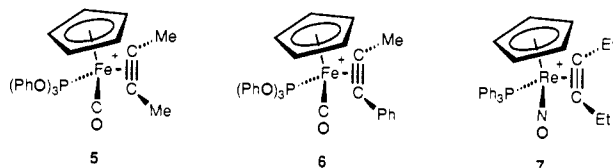
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Table V. Structures of Mononuclear Transition Metal η^2 -Ethyne Complexes

complex	M-C1 (Å)	M-C2 (Å)	C1-C2 (Å)	C1-H1 (Å)	C2-H2 (Å)	C1-M-C2 (deg)	C1-C2-H2 (deg)	C2-C1-H1 (deg)
[Mo(η^2 -HC≡CH)(Me ₃ CN≡C) ₂ (SCMe ₃) ₂] ^{28,29}	2.04 (2)	2.05 (2)	1.28 (2)	0.9 (2)	0.8 (2)	36.5 (7)	148 (10)	152 (13)
[W(η^2 -HC≡CH)(CO)(S ₂ CNEt ₂) ₂] ³¹	2.038 (8)	2.015 (9)	1.29 (1)				130 (6)	136 (4)
[W(η^2 -HC≡CH)Cl ₂ (MeC≡N) ₃][WOC ₄ (MeC≡N)] ³²	2.14 (3)	2.16 (4)	1.37 (5)			37 (1)		
[Ru(η^2 -HC≡CH)(PMe ₂ Ph) ₂ (Cp)][BF ₄]	2.20 (2)	2.21 (2)	1.22 (2)			32.2 (5)		
[Ni(η^2 -HC≡CH)(PPh ₃) ₂] ³⁴	1.873 (3)	1.882 (3)	1.239 (4)	0.921	0.979	38.53	146.6	149.4
[Cu(η^2 -HC≡CH)[HN(2-C ₂ H ₄ N) ₂]][BF ₄] ^{35,36}	1.97 (4)	1.97 (4)	1.19 (1)	0.923	0.923	35.1 (3)	164 (3)	164 (3)

Structure. Only one structure of a simple, mononuclear η^2 -alkyne complex of ruthenium has been reported in the Cambridge Structural Database.^{37,38} In this complex, [Ru(η^2 -MeO₂CC≡CCO₂Me)(NH₃)₅][PF₆]₂,³⁹ the Ru—C (2.117 (6) and 2.144 (5) Å) distances are slightly shorter, and the C≡C (1.238 (7) Å) distance is slightly longer, than those in **2**. The differences may be simply due to the strong electron-withdrawing nature of the MeO₂CC≡CCO₂Me ligand. Structural parameters of mononuclear, unsubstituted η^2 -ethyne complexes are collected in Table V.

A few structures of substituted η^2 -alkyne complexes with electronically similar [ML₂(Cp)]⁺ metal centers have been reported. In two related iron alkyne complexes, [Fe(η^2 -MeC≡CR)(CO)[P(OPh)₃](Cp)][SbF₆] (R = Me (**5**), Ph (**6**)),⁴⁰ and one rhenium complex, [Re(η^2 -C₂H₅C≡CC₂H₅)(NO)(PPh₃)(Cp)][BF₄] (**7**), respective C≡C distances of 1.19 (1), 1.21 (1), and 1.24 (1) Å are not significantly different from the 1.22 (2) Å distance in **2**. Gervasio and co-workers have suggested that the alkyne C—C bond length is a measure of effective back-bonding in metal-alkyne complexes,⁴¹ although this criterion should be used cautiously.^{22,31} The C≡C bond lengths in **2** and **5–7** are slightly longer than 1.203 Å for free ethyne, consistent with weak metal to alkyne π -back-bonding. In d⁴, group 6 metal complexes of the type [M(RC≡CR)LL'(Cp)]⁺, the alkyne formally donates four electrons to the metal.²² Alkyne π_{\perp} to metal σ , alkyne π_{\parallel} to metal d_x, and metal d_x to alkyne π_{\parallel}^* bonding are all significant in four-electron alkyne complexes, leading to longer alkyne C≡C distances, e.g., 1.29 (2) Å in [Mo(PhC≡CPh)(CO)(PPh₃)(Cp)][BF₄],³⁰ 1.291 (7) Å in [Mo(MeC≡CMe)(CO)(PEt₃)(η -C₅H₇)]⁴² and 1.31 (1) Å in [Mo(MeC≡CMe)(PMe₃)₂(η -C₅H₇)]⁴². Because the positions of the alkyne hydrogens could not be determined in the structure of **2**, the C≡C—H deformation angles were not established.



The orientation of the alkyne ligand in [M(RC≡CR)LL'(Cp)]⁺ complexes is also of interest. As illustrated in Figure 3, the η^2 -HC≡CH ligand in **2** is roughly perpendicular to the pseudosymmetry plane of the [Ru(PR₃)₂(Cp)] moiety. The dihedral angle between the Cp0—M—Mp (Cp0 is the cyclopentadienyl centroid, M is the metal atom, and Mp is the midpoint of the alkyne triple bond) and M—C1—C2 (C1 and C2 are the two bound alkyne carbons) planes is a measure of the deviation

of the alkyne ligand from a perpendicular orientation. For compounds **2**, **5**, **6**, and **7**, these angles are 81.6°, 89.9°, 85.3°, and 60.8°. Another measure of this asymmetry is a comparison of the Cp0—M—Mp—C1 and Cp0—M—Mp—C2 torsion angles, which would be 90° and -90° for an ideally perpendicular alkyne. For compounds **2**, **5**, **6**, and **7**, these pairs of torsion angles are (98.5°, -81.7°), (89.9°, -90.1°), (94.7°, -85.3°), and (60.8°, -119.2°), respectively. Thus, the ethyne ligand in **2** deviates more from a perpendicular orientation than the alkynes in iron compounds **5** and **6**, but the deviation in **7** is even greater. The perpendicular orientation is sterically favored, minimizing contact between the alkyne and the ancillary ligands. For symmetric, 16-electron [M(CO)₂(Cp)]⁺ (and presumably [M(PR₃)₂(Cp)]⁺) groups, calculations suggest that the perpendicular orientation of the alkyne is also electronically favored.^{12,21,43,44} For unsymmetrical, 16-electron [M(CO)(PR₃)(Cp)]⁺ or [M(NO)(PR₃)(Cp)]⁺ metal centers,^{12,23,24,40,44-46} metal d_x to alkyne π_{\parallel}^* orbital overlap is maximized when the alkyne is nearly aligned with the M—L vector of the better donor ligand, i.e., when one of the P—M—Mp—(alkyne carbon) torsion angles is near 0°. In the structures of **2**, **5**, **6**, and **7**, the smallest P—M—Mp—(alkyne carbon) torsion angles are 35.2°, 45.6°, 50.4°, and 10.9°, respectively. These data suggest that the orientations of the alkyne ligands in the iron and ruthenium complexes **2**, **5**, and **6** are determined mainly by steric factors, whereas in rhenium complex **7** electronic factors including metal d_x to alkyne π_{\parallel}^* orbital overlap are more significant. This is in accord with other spectroscopic and structural data.

The structure of [Ru(C=CH₂)(PMe₂Ph)₂(Cp)][BF₄] (**4**) is typical of a ruthenium(II) vinylidene complex. The Ru—C bond lengths of eight [Ru(C=CR₂)(PR'₂)(Cp)]⁺ structures⁴⁷⁻⁵³ in the Cambridge Crystallographic Database^{37,38} range from 1.824 to 1.864 Å (mean 1.843 (12) Å). The C1—C2 bond lengths range from 1.253 to 1.339 Å (mean 1.303 (26) Å), and the Ru—C1—C2 angles range from 165.8° to 179.9° (mean 172.8 (43)°). Bonding parameters of complex **4** fall near the mean in each case. Because the positions of the alkyne hydrogens could not be determined in the structure of **4**, the rotational orientation of the C=CH₂ ligand was not established. Compound **4** is the first ethynylidene (unsubstituted vinylidene) complex whose structure has been reported.

Summary. It is possible to isolate d⁶, η^2 -ethyne complexes of the type [Ru(η^2 -HC≡CH)(PR'₃)₂(Cp)]⁺ where PR'₃ has a small steric profile. In particular, [Ru(η^2 -HC≡CH)(PMe₂Ph)₂(Cp)][BF₄] (**2**) smoothly rearranges to its vinylidene isomer [Ru(C=CH₂)(PMe₂Ph)₂(Cp)][BF₄] (**4**) above ca. 60 °C in

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acetone solution. Structures of both **2** and **4**, determined by X-ray diffraction, are nearly identical except for the geometries of the C₂H₂ ligands.

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Supplementary Material Available: Tables of positional parameters and equivalent *B* values, anisotropic displacement parameters, complete bond distances and bond angles, least-squares planes, and torsion angles (12 pages); experimental and calculated structure factors for the structures of **2** and **4** (26 pages). Ordering information is available on any current masthead page.

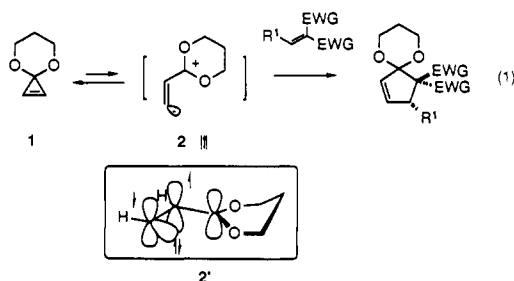
Thermal Reactions of Substituted Cyclopropenone Acetals. Regio- and Stereochemistry of Vinylcarbene Formation and Low-Temperature [3 + 2] Cycloaddition[†]

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Abstract: Cyclopropenone acetals bearing olefinic substituents of diverse electronic character have been synthesized and examined for their thermal behavior toward water and electron-deficient olefins. The substituted cyclopropenes underwent regio- and stereoselective hydration to give acrylate derivatives via vinylcarbene species, providing new data on the regio- and stereochemistry of vinylcarbene species. They also underwent regioselective [3 + 2] cycloadditions to electron-deficient olefins to give a variety of cyclopentenone acetals. In particular, phenylthio and ester substituents connected to the cyclopropene carbon effected highly regioselective vinylcarbene formation below room temperature to permit the thermal [3 + 2] cycloaddition to take place under extremely mild conditions.

Reversible generation and thermal [3 + 2] cycloaddition of the singlet vinylcarbene **2** under mild thermal conditions (70–80 °C) is an extremely unique reaction (eq 1).¹ Boger's extensive synthetic and mechanistic studies have revealed some useful and unusual characteristics of the reaction.² Synthetically, the reaction in eq 1 represents one of a few all-carbon thermal [3 + 2] cycloaddition reactions³ that is synthetically viable for the preparation of five-membered carbocycles and may serve as a complement to the Diels–Alder reaction. Among the various types of reactions available to vinylcarbenes,⁴ Boger's cycloaddition reaction (eq 1) represents the only example of the [3 + 2] cycloaddition of vinylcarbene species.⁵ Typical thermal reactions of vinylcarbenes include intramolecular rearrangement (e.g., CH insertion)⁶ or ring closure to cyclopropenes and occasional participation in [1 + 2] cycloaddition reactions.^{7,8} The ab initio calculations with electron correlation^{2a} indicate that the carbene **2** is most stable in its planar closed-shell singlet, π -delocalized form **2'**, which is consistent with the experimental behavior of the intermediates.



Although the cycloaddition of **1** is a synthetically powerful and mechanistically stimulating reaction, further extension of the chemistry beyond the currently established level has been difficult owing to the lack of substituted derivatives of **1**. This situation

has recently changed, as a variety of cyclopropenone acetals **5** and **7** are now available by the reaction of stable metal salts **4** and **6** with electrophiles (eq 2).¹⁰ The neopentyl glycol acetals **3**,

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