

# Synthesis and Properties of Ferrocenyl Allenylidene Complexes: X-ray Structure of [Ru(C=C=CHFc)(PPh<sub>3</sub>)<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)][PF<sub>6</sub>]·CH<sub>2</sub>Cl<sub>2</sub>

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Reactions of the transition metal halide complexes  $[MXL_2(Cp)]$  (M = Fe, X = I, L<sub>2</sub> = dppe; M = Ru, X = Cl, L = PPh<sub>3</sub>; M = Os, X = Br, L = PPh<sub>3</sub>; Cp =  $\eta$ -C<sub>5</sub>H<sub>5</sub>) with the alkynol HC=CCH(OH)(Fc) (1) (Fc = ferrocenyl) in the presence of TlBF<sub>4</sub> gave the monosubstituted allenylidene complexes  $[M(C=C=CHFc)L_2(Cp)][BF_4]$  (2a: M = Ru, L = PPh<sub>3</sub>; 3: M = Fe, L<sub>2</sub> = dppe; 4: M = Os, L = PPh<sub>3</sub>). Similarly, the reaction of 1 with  $[RuCl(PPh_3)_2(Cp)]$  and NH<sub>4</sub>PF<sub>6</sub> in methanol gave  $[Ru(C=C=CHFc)(PPh_3)_2(Cp)][PF_6]$  (2b). These highly colored compounds were characterized by spectroscopic and electrochemical techniques and in the case of 2b by a single-crystal X-ray structure determination. Cyclic voltammetry in MeCN in the presence of  $[^nBu_4N][ClO_4]$  at 100 mV · s<sup>-1</sup> shows a reversible ferrocenyl-based one-electron oxidation, in addition to irreversible oxidation and reduction processes. The NMR spectra of 2b show complex behavior at low temperature, attributed to temperature-dependent chemical shifts and correlated motions of the allenylidene ligand and the ferrocenyl substituent.

### Introduction

The first transition metal allenylidene complexes, [CpMn-(CO)<sub>2</sub>=C=C=C(<sup>t</sup>Bu)<sub>2</sub>] and [M(CO)<sub>5</sub>=C=C=C(Ph)NMe<sub>2</sub>] (M = Cr, W), were independently isolated by Berke<sup>1</sup> and Fischer,<sup>2</sup> respectively, reported in 1976, a decade after the first carbene<sup>3</sup> and vinylidene<sup>4</sup> homologues. Research to date on higher order cumulenylidene complexes has been hampered on account of synthetic challenges and the instability of products, although a number of butatrienylidene and pentatetraenylidene complexes have been reported, <sup>5-9</sup> and only very recently have the very first examples of heptahexaenylidene complexes, [(CO)<sub>5</sub>M=C(=C)<sub>5</sub>=C(NMe<sub>2</sub>)<sub>2</sub>] (M = Cr, W), been characterized.<sup>10</sup> The literature of allenyl-

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idene complexes has been comprehensively assessed by Bruce through 1998,<sup>11,12</sup> and Cadierno et al. to date,<sup>13,14</sup> with additional reviews appearing in the form of annual surveys<sup>15–19</sup> and metal-specific reviews encompassing chromium and tungsten,<sup>20</sup> iridium,<sup>21</sup> rhodium,<sup>22</sup> manganese,<sup>23</sup> and ruthenium.<sup>9,24–26</sup> Several comparative density functional theory treatments of cumulenylidene complexes have also been described.<sup>27–30</sup>

The vast majority of allenylidene complexes are those stabilized by cationic ruthenium(II) centers, an observation predominantly ascribed to the general applicability of the synthetic methodology developed by us in 1982 for the first

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ruthenium allenylidene complex, [CpRu(PMe<sub>3</sub>)<sub>2</sub>=C=C= CPh<sub>2</sub>]PF<sub>6</sub>.<sup>31</sup> The mechanism involves dissociation of chloride from the ruthenium complex and subsequent activation of the terminal alkyne at the coordinatively unsaturated metal, followed by rearrangement to a hydroxy-vinylidene intermediate, from which dehydration affords the allenylidene complex. The stability of the hydroxy-vinylidene complex is proportional to the electron-releasing properties of the ruthenium moiety, with dehydration to an allenylidene complex requiring acid catalysis for very electron-rich metal centers.<sup>32-34</sup>

The major exception to the general applicability of this synthetic route exists in those cases where a hydrogen is present at the atom  $\alpha$  to the hydroxyl carbon of the propargylic alcohol proligand, in which case competitive  $C\gamma - C\delta$  dehydration of the hydroxy-vinylidene intermediate affords a mixture of the allenylidene and alkenyl-vinylidene complexes.35 Further complications may arise as a consequence, for example in the reaction of Me<sub>2</sub>C(OH)C=CH with [CpRuCl(PPh<sub>3</sub>)<sub>2</sub>], where the postulated coupling of an allenylidene and vinyl-vinylidene complex results in the formation of a dimeric complex.<sup>36</sup> In light of these issues a number of alternate syntheses of allenylidene complexes have been reported, the most pertinent including addition of a nucleophile to the  $C\gamma$  atom of a butatrienylidene complex;<sup>25,37</sup> oxidation of a  $\sigma$ -alkynyl complex, such as  $[CpRu(PPh_3)_2(C = C - (C_5Me_4) - \eta^5 - RuCp)];^{38,39}$ and protonation of a vinyl- $\sigma$ -alkynyl complex such as  $[CpRu(PPh_3)_2-C \equiv C-C(Me) = CH_2].^{40}$ 

One aspect of our long-standing interest in the synthesis, structure, and reactivity of metallacumulenes<sup>31,36,41-45</sup> is the preparation of new allenylidene complexes. We report here that it is possible, with judicious choice of the allenylidene substituents, to stabilize monosubstituted allenvlidene complex cations ( $[L_nM=C=C=CHR]^+$ ) by favoring a propargyl cation resonance form (C and D, Figure 1).

Since ferrocenyl substituents effectively stabilize carbenium ions,  $[FcCR_2]^+$ ,<sup>46</sup> and carbon-rich metallacumulenes,<sup>47</sup> we have investigated the reactions of the ferrocenyl-functionalized secondary alkynol, HC=CCH(OH)(Fc) (1), with some group VIII transition metal halides, anticipating that the

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Figure 1. Resonance forms applicable to a transition metal allenylidene complex.

resulting ferrocenyl allenylidene cations would be stable (this work was preliminarily reported).<sup>48</sup>

A number of ferrocenyl-functionalized allenylidene complexes derived from tertiary alkynol proligands have been reported in the literature. $^{49-55}$  To the best of our knowledge, the only other analogous mononuclear example is the fullerene-substituted complex  $[(\eta^5-C_{60}Me_5)Ru-(1,2-dppp){C_3(H)Fc}]PF_6$ ,<sup>56</sup> where the crystallographic characterization is somewhat fraught by problems. Other salient complexes include a tetranuclear molybdenum complex, derived from  $[Fe{\eta^5-C_5H_4C(H)(OH)(C=CH)}_2]$ ,<sup>57</sup> in which two ferrocenyl allenylidene ligands bridge dimolybdenum moieties. Monosubstituted vinylidene ruthenocenyl complexes have also been prepared,<sup>38,39</sup> while the oxidation of  $[CpRu(PPh_3)_2-C \equiv C-Fc]$  leads to a fulvenyl-allenylidene complex.58

Subsequently, there have been a number of other monosubstituted allenylidenes prepared and structurally characterized.59-62

## **Experimental Section**

General Procedures. All reactions and manipulations were carried out under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques or in Vacuum Atmospheres

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HE43-2 or Braun MB-120 gloveboxes. Solvents were purified and dried under nitrogen by using standard techniques and transferred to reaction vessels via cannula or syringe. Melting points were measured in sealed capillaries. Microanalyses were performed by the Canadian Microanalytical Service, Delta, British Columbia.

**Instrumentation.** Infrared spectra were recorded as Nujol mulls on NaCl plates with a Perkin-Elmer 1710 FT-IR spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Varian Gemini 200 or Varian VXR-400 spectrometers and were referenced to the incompletely deuterated solvent peak. <sup>31</sup>P NMR spectra were recorded on either Varian VXR-400 or VXR-500 spectrometers operating at 162 and 202 MHz, respectively. The <sup>31</sup>P{<sup>1</sup>H} variable-temperature NMR studies were conducted on a Bruker ARX 500, and <sup>31</sup>P chemical shifts are reported in ppm downfield from external H<sub>3</sub>PO<sub>4</sub>. FAB mass spectra were obtained at the Mass Spectrometry Facility of the Ohio State University. A drop of the complex dissolved in CH<sub>2</sub>Cl<sub>2</sub> (ca. 0.5 M) was added to a drop of 3-nitrobenzyl alcohol matrix, and the mixture was applied to the probe tip.

Electrochemistry. Cyclic voltammetry was performed with a BAS-100A electrochemical analyzer. The cell consisted of two compartments separated by a porous glass frit to prevent crosscontamination of oxidation and reduction products. Platinum was used for both the working (disk) and auxiliary (wire) electrodes; a silver wire was used as a pseudoreference electrode. Each cell compartment was equipped with glass ground joints, a Teflon stopcock, and septum ports so that samples could be handled anaerobically. A 1.0 M solution of ["Bu<sub>4</sub>N][ClO<sub>4</sub>] in CH<sub>3</sub>CN was used as supporting electrolyte; sample concentrations were ca. 1 mM. Voltammograms were recorded at 25 °C by using a scan rate of  $100 \text{ mV} \cdot \text{s}^{-1}$ . Potentials are reported in mV relative to internal ferrocene(0/+). The criterion for diffusion control was  $i_p/v^{1/2}$  = constant, with variation of v between 100 and 500 mV  $\cdot$  s<sup>p<sub>1</sub>-1</sup>. Criteria for reversibility were as follows: (given for an oxidation process)  $i_{pa}/i_{pc} = 1.0$  reversible;  $i_{pa}/i_{pc} < 1.2$ near reversible;  $i_{pa}/i_{pc} > 1.2$  quasi-reversible; no apparent cathodic peak, irreversible.

**Starting Materials.**  $[RuCl(PPh_3)_2(Cp)]$ ,<sup>63</sup>  $[OsBr(PPh_3)_2(Cp)]$ ,<sup>64,65</sup> and  $[FeI(dppe)(Cp)]^{66}$  were prepared by known methods. A slight modification of the literature procedure,<sup>67</sup> replacing NaC=CH with LiC=CH in THF,<sup>68,69</sup> was used to prepare HC=CCH(OH)(Fc). [<sup>n</sup>Bu<sub>4</sub>N][ClO<sub>4</sub>] (Southwestern Analytical) and NH<sub>4</sub>PF<sub>6</sub> (Ozark-Mahoning) were used as received.

**Preparation of [Ru(C=C=CHFc)(PPh<sub>3</sub>)<sub>2</sub>(Cp)][BF<sub>4</sub>] (2a).** A mixture of [RuCl(PPh<sub>3</sub>)<sub>2</sub>(Cp)] (300 mg, 0.413 mmol), HC≡ CCH(OH)(Fc) (141 mg, 0.587 mmol), and TlBF<sub>4</sub> (173 mg, 0.594 mmol) in THF (20 mL) was stirred at ambient temperature for 1 h. The resulting dark green solution was filtered through a Celite pad (1 × 3 cm), and the pad was eluted with THF until the eluate was colorless. The filtrate was concentrated to ca. 5 mL, and Et<sub>2</sub>O (ca. 60 mL) was added by syringe to precipitate a dark green powder. The solvent was decanted from the solid by cannula, and the solid was washed with additional Et<sub>2</sub>O (2 × 20 mL) to give **2b** (323 mg, 78%). Mp > 150 °C (dec). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ (ppm) 8.96 (s, 1H, H3), 7.50−7.20 (m, 30H, phenyl), 5.37 (t, 2H, H6,7, <sup>3</sup>J<sub>H,H</sub> = 1.9 Hz), 5.11 (t, 2H, H5,8), 5.08 (s, 5H, ring A), 4.36 (s, 5H, ring B). {<sup>1</sup>H} <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ (ppm) 271.5 (t, C1, <sup>2</sup>J<sub>P,H</sub> = 20 Hz), 182.6 (s, C2), 152.5 (s, C3), 135.8−128.2 (m, phenyl), 91.8 (s, ring A), 90.6 (s, C4), 78.9

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(s, C5,8 and C6,7), 72.7 (s, ring B).  ${}^{1}H{}^{31}P$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) 47.5. IR (cm<sup>-1</sup>): 1943 (vs, C=C=C), 1585 (w), 1571 (w), 1435 (s), 1352 (s), 1312 (s), 1282 (m), 1256 (m), 1185 (m), 1159 (m), 1089 (s), 1050 (vs, BF), 998 (m), 923 (w), 834 (w), 744 (w), 722 (w), 696 (s), 618 (w).

Preparation of [Ru(C=C=CHFc)(PPh<sub>3</sub>)<sub>2</sub>(Cp)][PF<sub>6</sub>] (2b). A mixture of [RuCl(PPh<sub>3</sub>)<sub>2</sub>(Cp)] (224 mg, 0.309 mmol), HC≡ CCH(OH)(Fc) (135 mg, 0.562 mmol), and NH<sub>4</sub>PF<sub>6</sub> (57 mg, 0.350 mmol) in MeOH (20 mL) was stirred at ambient temperature for 2.5 h. The resulting emerald-green solution was evaporated to dryness, and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (ca. 7 mL) and filtered. Addition of Et<sub>2</sub>O (ca. 100 mL) to the filtrate and stirring for 2 h resulted in the precipitation of a dark green powder of **2b** (235 mg, 72%). An analytical sample was obtained by vapor diffusion of isopentane into a CH<sub>2</sub>Cl<sub>2</sub> solution of **2b** and drying in vacuo for 3 days. Anal. Calcd for C54H45F6Fe-P<sub>3</sub>Ru: C, 61.31; H, 4.29. Found: C, 61.42; H, 4.29. Mp > 150 °C (dec). <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>CO):  $\delta$  (ppm) 8.79 (s, 1H, H3), 7.20– 6.99 (m, 30H, phenyl), 5.00 (t, 2H, H6,7,  ${}^{3}J_{H,H} = 1.8$  Hz), 4.80 (t, 2H, H5,8), 4.73 (s, 5H, ring A), 4.07 (s, 5H, ring B). {<sup>1</sup>H}<sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) 273.0 (t, C1, <sup>2</sup>J<sub>P,H</sub> = 21 Hz), 183.7 (s, C2), 153.3 (s, C3), 136.7–128.8 (m, phenyl), 92.4 (s, ring A), 91.2 (s, C4), 79.4 (s, C5,8 and C6,7), 73.1 (s, ring B).  ${}^{1}H{}^{31}P$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) 47.9. IR (cm<sup>-1</sup>): 1940 (vs, C=C=C), 1732 (m), 1678 (w), 1651 (w), 1489 (s), 1435 (s), 1435 (s), 1357 (w), 1270 (w), 1258 (m), 874 (m), 839 (vs, br, PF), 758 (w), 741 (m), 723 (w), 699 (s). FAB MS: 913 ( $[M]^+$ , 31%); 792 ([M - Fe- $(C_5H_5)]^+$ , 26%); 651 ([M - PPh<sub>3</sub>]<sup>+</sup>, 24%); 585 ([M - PPh<sub>3</sub> - $C_5H_6$ ]<sup>+</sup>, 12%); 529 ([Ru( $C_3HC_5H_4$ )(PPh<sub>3</sub>)( $C_5H_5$ )]<sup>+</sup>, 6%); 429  $([Ru(PPh_3)(C_5H_5)], 100\%).$ 

Preparation of [Fe(C=C=CHFc)(dppe)(Cp)][BF<sub>4</sub>] (3). A mixture of [FeI(dppe)(Cp)] (112 mg, 0.466 mmol), HC=CCH(OH)-(Fc) (112 mg, 0.466 mmol), and TlBF<sub>4</sub> (252 mg, 0.865 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was stirred at ambient temperature for 12 h. The resulting deep purple mixture was evaporated to dryness, and the residue was washed with  $Et_2O(3 \times 20 \text{ mL})$ . The residue was extracted with CHCl<sub>3</sub> (ca. 5 mL) and filtered through Celite. Slow addition of Et<sub>2</sub>O (ca. 60 mL) to the filtrate precipitated a deep purple powder of 4 (180 mg, 70%). Anal. Calcd for C44H39BF4Fe2P2: C, 63.80; H, 4.74. Found: C, 63.00; H, 4.65.  $Mp > 150 \text{ °C} (dec). ^{1}\text{H NMR} (CD_{2}Cl_{2}): \delta (ppm) 7.90 (t, 1H, H3, t)$  ${}^{5}J_{P,H} = 12$  Hz), 7.80–7.30 (m, 20H, phenyl), 5.20 (s, 5H, ring A), 4.89 (t, 2H, H6,7,  ${}^{3}J_{H,H} = 1.8 \text{ Hz}$ ), 4.68 (t, 2H, H5,8), 4.06 (s, 5H, ring B), 3.18 (vd, 4H, PC<sub>2</sub>H<sub>4</sub>P,  ${}^{2}J_{P,H} = 12 \text{ Hz}$ ). { ${}^{1}H{}^{13}C$ NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) 280.1 (t, Cl,  ${}^{2}J_{P,H} = 38 \text{ Hz}$ ), 198.2 (s, 62) C2), 146.2 (s, C3), 146.2-128.6 (m, phenyl), 89.6 (s, C4), 88.7 (s, ring A), 76.6 (s, C5,8 and C6,7), 71.7 (s, ring B), 29.8 (vt, PC<sub>2</sub>H<sub>4</sub>P,  ${}^{1}J_{P,C} = 22$  Hz).  ${}^{1}H{}^{31}P$  NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm) 100.8. IR (cm<sup>-1</sup>): 1934 (vs, C=C=C), 1651 (w), 1586 (w), 1309 (w), 1281 (w), 1261 (w), 1185 (w), 1050 (vs, br, BF), 866 (w), 840 (w), 830 (w), 822 (w), 799 (w), 752 (w), 710 (m), 697 (w). FAB MS: 741 ( $[M]^+$ , 100%); 676 ( $[M - (C_5H_5)]^+$ , 1.5%); 620  $([M - Fe(C_5H_5)]^+, 16\%).$ 

**Preparation of [Os(C=C=CHFc)(PPh<sub>3</sub>)<sub>2</sub>(Cp)][BF<sub>4</sub>] (4).** In a manner analogous to the preparation of **2b**, [OsBr(PPh<sub>3</sub>)<sub>2</sub>(Cp)] (203 mg, 0.236 mmol), HC≡CCH(OH)(Fc) (126 mg, 0.525 mmol), and TlBF<sub>4</sub> (340 mg, 1.17 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) gave a dark green powder of **3** (212 mg, 85%). Anal. Calcd for C<sub>54</sub>H<sub>45</sub>BF<sub>4</sub>Fe-P<sub>2</sub>Os: C, 59.57; H, 4.17. Found: C, 58.78; H, 4.58. Mp > 150 °C (dec). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ (ppm) 10.98 (s, 1H, H3), 7.40−7.10 (m, 30H, phenyl), 5.11 (s, 5H, ring A), 5.03 (t, 2H, H6,7, <sup>3</sup>J<sub>H,H</sub> = 1.7 Hz), 4.86 (t, 2H, H5,8), 4.16 (s, 5H, ring B). {<sup>1</sup>H} <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ (ppm) 246.5 (t, C1, <sup>2</sup>J<sub>P,H</sub> = 13 Hz), 195.1 (s, C2), 150.9 (s, C3), 137.5−128.8 (m, phenyl), 94.1 (s, C4), 90.7 (s, ring A), 77.6 (s, C5,8 and C6,7), 72.6 (s, ring B). {<sup>1</sup>H} <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ (ppm) 81.6. IR (cm<sup>-1</sup>): 1942 (vs, C=C=C), 1652 (m), 1586 (w), 1573 (w), 1481 (s), 1435 (s), 1352 (sh), 1313 (m), 1259 (m), 1186 (m), 1163 (m), 1080 (vs, br, BF) 925 (w), 836 (m), 823 (m), 747 (m), 697 (s).

**Crystallography.** X-ray quality crystals of **2b** were obtained by slow diffusion of isopentane into a dichloromethane solution at

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 Table 1. Summary of the Crystal Data and Details of Intensity

 Collection and Refinement for Complex 2b

Crys	tal Data
color and habit size (mm <sup>3</sup> ) formula fw Z $D_c$ (g cm <sup>-3</sup> ) a (Å) b (Å) c (Å) c (Å) $\alpha$ (deg) $\beta$ (deg) $\gamma$ (deg) $\gamma$ (deg) volume (Å <sup>3</sup> )	dark green, irregular ca. $0.6 \times 0.4 \times 0.3$ $C_{55}H_{47}Cl_2F_6FeP_3Ru$ 1142.714 2 $1.52_1$ 14.606(3) 15.260(5) 12.654(4) 107.40(3) 108.26(2) 95.83(2) 2495.73 1160
F(000) corrected	1158.878

#### Data Collection

radiation	Μο Κα
λ	0.710703 Å
temperature	23 °C
sets of setting angles refined	25
$\theta$ range for Cell	$3^{\circ}$ to $20^{\circ}$
maximum counting time	90 s
$\theta$ limits for data	2° to 22.5°
h, k, l ranges	0 to 15, -16 to 16, -13 to 13
scan type	$\omega - 2\theta$
scan range	$0.70 + 0.35 \tan \theta$
number of standards	3
maximum variation	5.2%
unique data	6819
data with $I \ge 3\sigma(I)$	5527
μ	$8.479 \text{ cm}^{-1}$
absorp corr	none

#### Structure Solution and Refinement

space group	<i>P</i> 1 (No. 2)
final number of variables	617
<i>p</i> factor	0.02
max. shift/error in last cycle	0.08 ( $\beta_{1,2}$ of C9)
R	3.8%
$R_{ m w}$	4.9%
error in observation of unit weight	2.9037
largest peak in final diff Fourier	0.091 e/Å <sup>3</sup> near C12

room temperature. A crystal was mounted on a glass fiber and coated with epoxy resin. All X-ray diffraction measurements were made by using an Enraf-Nonius CAD4 diffractometer. The unit cell was determined from 25 randomly selected reflections, which were recentered to obtain refined cell dimensions. Data were corrected for Lorentz and polarization effects. Corrections for extinction or absorption ( $\nu = 8.479 \text{ cm}^{-1}$ ) were not needed.

The ruthenium and iron atoms were located from a Patterson map, and the remaining non-hydrogen atoms were located by using DIRDIF<sup>70</sup> and difference Fourier methods. Data with I  $\geq 3\sigma(I)$  were used for the subsequent refinement of the structure using local versions of Ibers' NUCLS least-squares program (based on the Busing-Levy ORFLS), Zalkin's FORDAP Fourier program, and Johnson's ORTEP thermal ellipsoid plotting program.<sup>71</sup> Non-hydrogen atoms were refined by using anisotropic thermal parameters. Anomalous dispersion corrections were included for the scattering of Ru, Fe, P, and F. Least-squares refinements minimized the function  $\sum_{hkl} (F_o - F_c)^2$ , where the weighting factor was  $w = 1/\sigma(F_o)^2$ . The hydrogen atom H3 was located in a difference Fourier

map and included in least-squares refinement. The remaining hydrogen atoms were placed in idealized positions with d(C-H) = 1.0 Åand  $B = B(\text{attached C}) + 1.0 \text{ Å}^2$ ; their positions were adjusted after each cycle of refinement. Additional details of data collection and refinement are presented in Table 1.

#### **Results and Discussion**

**Synthesis.** The reaction of **1** with  $[RuCl(PPh_3)_2(Cp)]$  and TlBF<sub>4</sub> in dichloromethane gave a dark green solution, from which  $[Ru(C=C=CHFc)(PPh_3)_2(Cp)][BF_4]$  (**2a**, Scheme 1) was obtained in high yield. Dark green  $[Ru(C=C=CHFc)-(PPh_3)_2(Cp)][PF_6]$  (**2b**) was conveniently prepared by using NH<sub>4</sub>PF<sub>6</sub> in methanol. The TlBF<sub>4</sub> method was employed in the preparation of the analogous iron and osmium complexes  $[Fe(C=C=CHFc)(dppe)(Cp)][BF_4]$  (**3**) and  $[Os(C=C=CHFc)(PPh_3)_2(Cp)][BF_4]$  (**4**).

The TIBF<sub>4</sub> reactions are driven by the formation of insoluble thallium halides, which precipitate as the intense colors of the allenylidene cations develop. Traces of TIBF<sub>4</sub> were carried through the dichloromethane/ethyl ether recrystallizations; these were removed from microanalytical samples by filtration of concentrated chloroform solutions of the complexes. The green ruthenium (2) and osmium (4) and the deep purple iron (3) allenylidene complexes are air-stable as solids, but solutions are best handled under inert atmosphere. The complexes are soluble in polar solvents such as tetrahydrofuran, dichloromethane, and alcohols, but insoluble in diethyl ether and hydrocarbons.

A mechanism for the formation of the allenylidene complexes is shown in Scheme 1. The light-colored solutions encountered in the synthesis of complexes 2-4 probably contain an intermediate, either the  $\eta^2$ -alkyne complex **F** or the vinylidene complex **G**. The latter seems more likely, since  $[\operatorname{Ru}(\eta^2-\operatorname{HC}=\operatorname{CR})(L_2)(\operatorname{Cp})]^+$ complexes are detectable or isolable only for phosphine or phosphite ligands (L) of small cone angle and very small alkyne substituents ( $\mathbf{R} = \mathbf{H}$  or  $\operatorname{Me}$ ).<sup>42,66,72</sup> Rearrangement of **F** to **G** should be very rapid; the mechanism by which this occurs has been extensively studied and thought to occur by a 1,2-H shift<sup>42,66,72</sup> or via intra- or intermolecular proton transfer in an alkynyl-hydride intermediate.<sup>73</sup> Spontaneous loss of H<sub>2</sub>O from **G** gives the allenylidene complexes, **E**, in high yield. Acidpromoted hydroxide loss to give ferrocenyl-stabilized vinyl and allenyl cations is well-precedented.<sup>46,74-78</sup> The intermediacy of hydroxyvinylidene complexes leading to allenylidene complexes is consistent with many previous observations.<sup>13,31,32,36,49,50,79-90</sup>

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In contrast,  $[OsCl(P^{i}Pr_{3})_{2}(Cp)]$  reacts with alkynols to give  $[OsCl\{\eta^{2}-HC\equiv CC(OH)R_{2}\}(P^{i}Pr_{3})(Cp)]$  (R = Ph, Me), which rearrange and dehydrate in toluene to give allenylidene  $[OsCl\{C=C=CPh_{2}\}(P^{i}Pr_{3})(Cp)]$  or vinylvinylidene  $[OsCl\{C=C+CPh_{2}\}(P^{i}Pr_{3})(Cp)]$  complexes or react with TlPF<sub>6</sub> to give stable, cationic complexes with four-electron alkyne ligands,  $[Os\{\eta^{2}-HC\equiv CC(OH)R_{2}\}(P^{i}Pr_{3})(Cp)][PF_{6}]^{.91}$ 

We were not able to isolate pure ruthenium allenylidene complexes containing PMe<sub>3</sub> or dppe ligands. In the latter case, the presence of relatively large amounts of impurities prevented the complete characterization of the dark green complex obtained; FAB mass spectrometry suggested that [Ru(C=C= CHFc)(dppe)(Cp)][BF<sub>4</sub>] was the principal product. Cadierno et al. similarly reported that [RuCl(PPh<sub>3</sub>)<sub>2</sub>( $\eta^{5}$ -indenyl)] reacts with HC=CH(OH)(Ph) and NaPF<sub>6</sub> to give stable [Ru(C=C= CHPh)(PPh<sub>3</sub>)<sub>2</sub>( $\eta^{5}$ -indenyl)][PF<sub>6</sub>], whereas the allenylidene complexes derived similarly from [RuClL<sub>2</sub>( $\eta^5$ -indenyl)] (L<sub>2</sub> = dppm, dppe) are unstable toward MeOH.<sup>87</sup> The reaction of  $[RuCl(PMe_3)_2(Cp)]$  and TlBF<sub>4</sub> or NH<sub>4</sub>PF<sub>6</sub> with 1 in THF or CH<sub>2</sub>Cl<sub>2</sub> gave a complex mixture of products (by <sup>1</sup>H NMR). Perhaps the PMe<sub>3</sub> ancillary ligands are too small to effectively shield the allenylidene ligand from nucleophilic attack in putative  $[Ru(C=C=CHFc)(PMe_3)_2(Cp)]^+$ .

**Spectroscopic Characterization.** Ferrocenyl allenylidene complexes **2**, **3**, and **4** were unambiguously characterized by spectroscopic methods. In fast atom bombardment (FAB) mass spectra of complexes **2b** and **3**, molecular cations were found at m/z 913 and 741, respectively, which fragment by loss of [Fe(C<sub>5</sub>H<sub>5</sub>)]. The infrared spectra of complexes **2–4** show intense bands at ca. 1940 cm<sup>-1</sup>, confirming the presence of the allenylidene moiety.<sup>12</sup>

There has been theoretical and experimental interest in the properties of  $C_3H_2$  species.<sup>14,92</sup> Vinylidenecarbene,  $H_2C=C=C$ :,

was calculated to have a singlet ground state. Comparison of computed vibrational frequencies with experimentally derived IR intensities suggested that the intense band at ca. 2000 cm<sup>-1</sup> is an antisymmetric CC stretching mode. The intensity of the band was ascribed to a large change in dipole moment as a result of oscillation between limiting structures  $H_2C=C=C$ : and  $H_2C^+$ . C=C:<sup>-</sup>, respectively. Such arguments may explain the intensity of the bands at ca. 1900 cm<sup>-1</sup> in the infrared spectra of complexes **2–4**.

In the <sup>1</sup>H NMR spectra of complexes **2**, **3**, and **4** (Table 2), the allenylidene hydrogen (H3,  $[M=C=C=CHFc]^+$ ) resonates downfield ( $\delta 8-11$ ) in the region typical of hydrogen atoms on carbenium ions or metal alkylidene ligands.<sup>93,94</sup> The allenylidene hydrogen resonates furthest downfield for osmium compound **4** and furthest upfield for iron compound **3**. This trend may reflect the decreasing  $\pi$ -donating ability of the  $[ML_2(Cp)]$  fragments on descending the group, suggesting that the propargyl cation resonance form **B** decreases in importance from osmium to iron. Cadierno et al. reported a similar <sup>1</sup>H NMR shift of  $\delta 9.09$  for the allenylidene hydrogen of  $[Ru(C=C=CHPh)(PPh_3)_2(\eta^5-indenyl)][PF_6].^{87}$ 

The [ML<sub>2</sub>(Cp)] cyclopentadienyl resonance is downfield of the ferrocenyl cyclopentadienyl resonance, reflecting the substantial positive charge localized at [ML<sub>2</sub>(Cp)]. Only for iron complex 3 does the cyclopentadienyl resonance show  ${}^{1}\text{H}-{}^{31}\text{P}$  coupling to the phosphine ligands; phosphorus-toligand J coupling is typically larger for Fe than for Ru or Os. The shifts of the  $C_5H_4$  group proved difficult to assign. The H3,4 protons of  $[Fe(\eta^{5}-C_{5}H_{4}CH_{2})(\eta^{5}-C_{5}H_{5})]^{+}$  (5, Scheme 2) and related  $\alpha$ -ferrocenylcarbenium ions are found at lower field than the H2,5 protons.<sup>46</sup> However, Connor assigned the H2,5 protons at lower field than the H3,4 protons in neutral, ferrocenyl Fischer-type carbene complexes of group VI metals (6),<sup>95</sup> in which the carbon carbon bears a partial positive charge. The C<sub>5</sub>H<sub>4</sub> shifts of complexes 6 were assigned by analogy to other Fischer-type carbene complexes containing electron-withdrawing groups.<sup>95</sup> The H2,5 and H3,4 resonances were not specifically assigned in the ferrocenyl carbyne complexes (7).<sup>96</sup> We were not able to unequivocally assign the

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Table 2. <sup>1</sup>H and <sup>31</sup>P NMR Data for the Allenylidene Complexes

	$\frac{{}^{1}\mathrm{H}}{\mathrm{ppm}} (\mathrm{multiplicity}, {}^{3}J_{\mathrm{H,H}} (\mathrm{Hz}))$						<sup>31</sup> P	
	H3	H5,8	H6,7	ring A	ring B	phenyl		
$2a^{a} 2b^{b} 3^{a,c} 4^{b}$	8.96 (s) 8.79 (s) 7.90 (t, 2.4) <sup>d</sup> 10.98 (s)	5.11 (t, 1.9) 4.80 (t, 1.8) 4.68 (t, 1.8) 4.86 (t, 1.7)	5.37 (t, 1.9) 5.00 (t, 1.8) 4.89 (t, 1.8) 5.03 (t, 1.7)	5.08 (s) 4.73 (s) 5.20 (s) 5.11 (s)	4.36 (s) 4.07 (s) 4.06 (s) 4.16 (s)	7.20-7.50 (m) 6.99-7.20 (m) 7.30-7.80 (m) 7.10-7.40 (m)	47.5 47.9 100.8 81.6	

 ${}^{a}$ CD<sub>2</sub>Cl<sub>2</sub>.  ${}^{b}$ (CD<sub>3</sub>)<sub>2</sub>CO.  ${}^{c}$ dppe CH<sub>2</sub>  $\delta$  3.18 (vd),  ${}^{2}J_{P,H} = 12$  Hz.  ${}^{d}$   ${}^{5}J_{P,H} = 12$  Hz.

ferrocenyl resonances of 2-4, even with the extensive application of 2-D NMR techniques. We favor the assignment of the lower field triplets of 2-4 to protons H5,8 and the higher field signal to H6,7, based on analogy to the  $\alpha$ -ferrocenylcarbenium ion 5. Connor and Lloyd used empirical linear relationships between (a) the Hammett substituent constant,  $\sigma_{\rm P}$ , and  $\Delta_{2.5}$  and also between (b) the resonance substituent constant,  $\sigma_{\rm R}$ , and the value of  $(\Delta_{3,4} - \Delta_1)$  as an indication of the overall and the resonance electron-withdrawing abilities of the alkylidene substituent in compounds 6.95 Fischer and co-workers derived similar Hammett  $\sigma$  values from NMR and electrochemical data for compounds 7.96 By using Connor's empirical relationships, we find  $\sigma_{\rm P}$  values of +0.75, +0.52, +0.46, and +0.49 and  $\sigma_{\rm R}$  values of +1.00, +1.16, +1.03, and +1.06 for the  $[M(C_3H)(L)_2(Cp)]^+$  substituents in compounds **2a**, **2b**, **3**, and **4**, respectively.<sup>97</sup> Both the <sup>1</sup>H shifts themselves and the derived Hammett  $\sigma$  values make it clear that the  $[M(C_3H)(L)_2(Cp)]^+$  substituents are strongly electron-withdrawing, especially through the delocalized  $\pi$ -system rather than through inductive effects. However, the large solvent dependence of the <sup>1</sup>H NMR shifts of **2a** in CD<sub>2</sub>Cl<sub>2</sub> and **2b** in  $(CD_3)_2CO$ , and the uncertainty in the H5,8 versus H6,7 assignments, make the derived  $\sigma$  values quantitatively worthless. Clearly, the  $[M(C_3H)(L)_2(Cp)]^+$  substituents are more strongly electron-withdrawing than either the alkylidene substituents in 6 or the alkylidyne substituents in 7, probably because of the overall positive charge of compounds 2-4.

In the <sup>13</sup>C NMR spectra of complexes **2**–**4** (Table 3), phosphorus-coupled triplets assigned to C1 are found at low field ( $\delta$  245 to 280 ppm). C1 of the iron complex **3** resonates at lowest field, and C1 of the osmium complex **4** at the highest field. Carbon atoms C2 resonate between  $\delta$  180 and 200 ppm, characteristic of the internal, sp-hybridized carbon atoms of allenes<sup>98</sup> and other allenylidene complexes.<sup>11,31,99</sup> Carbon atoms C3 resonate between  $\delta$  145 and 155 ppm, downfield of the usual  $\delta$  75 to 120 ppm range for terminal allene carbons.<sup>98</sup> This is evidence for cationic character, or a significant contribution of the paramagnetic chemical shift term due to a small HOMO–LUMO gap, at C3.<sup>100,101</sup> The <sup>13</sup>C{<sup>1</sup>H} NMR spectra of complexes **2**–**4** (Table 3) showed only two singlets of relative intensity ca. 1:4 at ca. 90 and



X = CI, Br, I.

ca. 78 ppm for the substituted ferrocenyl cyclopentadienyl ring. These peaks are assigned to C4 and the superimposition of C5,8 and C6,7, respectively. The shifts of C2,5 and C3,4 in complexes 7 are found at ca. 71 ppm, differing by only ca. 1 ppm.<sup>96</sup> The remaining cyclopentadienyl and phenyl resonances of complexes 2-4 are found at predictable shifts.

<sup>31</sup>P NMR Spectra. The <sup>31</sup>P NMR spectra of the allenylidene complexes 2-4 (Table 2) each display a singlet for the phosphine ligands at room temperature. The <sup>31</sup>P NMR spectrum of [Ru(C=C=CHFc)(PPh<sub>3</sub>)<sub>2</sub>(Cp)][PF<sub>6</sub>] (2b) shows complex temperature dependence. The <sup>31</sup>P NMR spectrum in  $CD_2Cl_2$  shows one singlet ( $\delta$  47.9) at room temperature. On cooling, the line initially broadens, and below 255 K two broad signals become apparent. These two signals sharpen to a clear AB pattern below 233 K (Figure 2). The <sup>31</sup>P NMR chemical shift of each of the components of the AB system shows a nearly linear temperature dependence between 238 and 190 K. In addition, the higher field <sup>31</sup>P signal at 233 K moves to a lower field position relative to its partner below 206 K, presumably due to changes in the phosphorus shifts, possibly via slight movements of phenyl rings affecting angles at phosphorus.

Each of the spectra that showed a clear AB pattern was simulated, initially by line assignment and subsequently by complete line-shape analysis,<sup>102</sup> in order to determine accurate chemical shifts, the <sup>31</sup>P-<sup>31</sup>P coupling constant of 29.5 Hz, and the pseudo-first-order rate constants for the exchange process in the temperature range 210–233 K. The linearity of the change in chemical shift with temperature allowed the determination of <sup>31</sup>P NMR chemical shifts in

<sup>(97)</sup>  $\Delta 2,5 = -147\sigma p + 13; (\Delta 3,4 - \Delta 1) = -81\sigma R + 0.8;$  where  $\Delta i,j = \delta$ (FcH)  $-\delta$ (Hi,j of complex) and  $\Delta 1 = \delta$ (FcH)  $-\delta$ (H unsubstituted Cp of complex). For comparison with Connor's values,  $\Delta i,j$  values are corrected to Hz for a 100 MHz <sup>1</sup>H spectrum.

<sup>(98)</sup> Levy, G. C.; Lichter, R. L.; Nelson, G. L. In *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*; Wiley: New York, 1980; pp 85–89.

<sup>(99)</sup> Bruce, M. I.; Swincer, A. G. Adv. Organomet. Chem. 1983, 22, 59–128.

<sup>(100)</sup> Czech, P. T.; Ye, X.-Q.; Fenske, R. F. Organometallics **1990**, 9, 2016–2022.

<sup>(101)</sup> Fenske, R. F. In *Organometallic Compounds: Synthesis, Structure and Theory*; Shapiro, B. L., Ed.; Texas A&M University Press: College Station, TX, 1983; pp 305–333.

<sup>(102)</sup> Adams, C. J.; Bruce, M. I.; Skelton, B. W.; White, A. H. Chem. Commun. 1996, 7, 2663–2664.

Table 3. <sup>13</sup>C NMR Data for the Allenylidene Complexes (CD<sub>2</sub>Cl<sub>2</sub> solution)

				ppm (multip	ultiplicity, ${}^{2}J_{P,C}$ (Hz))			
	C1	C2	C3	C4	C5,8 and C6,7	ring A	ring B	phenyls
2a	271.5(t, 20)	182.6(s)	152.5 (s)	90.6 (s)	78.9 (s)	91.8 (s)	72.7 (s)	128.2-135.8 (m)
2b	273.0(t, 21)	183.7 (s)	153.3 (s)	91.2(s)	79.4 (s)	92.4 (s)	73.1 (s)	128.8-136.7 (m)
$3^{a}$	280.1 (t, 38)	198.2(s)	146.2 (s)	89.6 (s)	76.6(s)	88.7 (s)	71.7(s)	128.6-146.2 (m)
4	246.5(t, 13)	195.1 (s)	150.9 (s)	94.1 (s)	77.6 (s)	90.7 (s)	72.6 (s)	128.8-137.5 (m)

<sup>*a*</sup> dppe CH<sub>2</sub>  $\delta$  29.8 (vt), <sup>1</sup>J<sub>P,C</sub> = 22 Hz.



Figure 2. Stacked plot of <sup>31</sup>P NMR variable-temperature experiment on compound 2b (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>).

each of the broadened spectra (238-263 K) by extrapolation. The extrapolated chemical shifts were employed as starting values in the simulation of each of the spectra, leading to pseudo-first-order rate constants. Some of the simulated and experimental spectra are depicted in Figure 3.

The rate constant ( $k_{\rm C}$ ) at the coalescence temperature ( $T_{\rm C} = 255 \text{ K}$ ) was also calculated by using eq 1.<sup>103</sup>

$$k_{\rm C} = 2.22 \sqrt{\Delta \nu^2 + 6J_{\rm AB}^2 \rm s^{-1}}$$
(1)

This equation gives a  $k_{\rm C}$  of 440 s<sup>-1</sup>, which is in good agreement with 430 s<sup>-1</sup> obtained from line-shape analysis. The barrier for the exchange process ( $\Delta G_{\rm C}^{\pm}$ ) was calculated to be 49.0(8) kJ mol<sup>-1</sup> by using eq 2.<sup>103</sup>

$$\Delta G_{\rm C}^{\ddagger} = 19.14 T_{\rm C} \left( 10.32 + \log \frac{T_{\rm C}}{k_{\rm C}} \right) \text{kJ mol}^{-1} \qquad (2)$$

Alternatively,  $\Delta G_{\rm C}^{\ddagger}$  was calculated to be 49.1(8) kJ mol<sup>-1</sup> by using eq 3.<sup>104</sup>

$$\Delta G^{\ddagger} = 19.14 T_{\rm C} \left( 9.97 + \log \frac{T_{\rm C}}{\delta \nu} \right) \text{kJ mol}^{-1} \qquad (3)$$

The parameters  $\Delta H^{\ddagger} = 50(3) \text{ kJ mol}^{-1}$  and  $\Delta S^{\ddagger} = 3 \pm 13 \text{ J K}^{-1} \text{ mol}^{-1}$  were determined by plotting log k/T vs 1/T according to eq 4.<sup>103,104</sup>

$$\log \frac{k}{T} = 10.32 - \frac{\Delta H^{\ddagger}}{19.14T} + \frac{\Delta S^{\ddagger}}{19.14}$$
(4)

We attribute this <sup>31</sup>P NMR temperature dependence to slow rotation of the allenylidene ligand about the RuC<sub>3</sub> axis, whereby the *anti* isomer exchanges with the corresponding *syn* isomer ( $k_{Ru}$ , Figure 4). Rotation of the ferrocenyl substituent with respect to the allenylidene plane,  $k_{Fe}$ , is apparently rapid, although some line broadening at low temperature may be due to slowing of ferrocenvl rotation.

Solid-State Structure of [Ru(C=C=CHFc)(PPh<sub>3</sub>)<sub>2</sub>(Cp)]- $[PF_6] \cdot CH_2Cl_2$  (2b). The molecular structure of the cation of **2b** is shown in Figure 5. The ruthenium atom displays a typical "three-legged piano stool" (pseudo-octahedral) coordination geometry, and structural parameters within the [Ru(PPh<sub>3</sub>)<sub>2</sub>(Cp)] moiety are typical. The C1-C2-C3 chain of the allenylidene ligand is roughly linear, adopting a "vertical" conformation with a dihedral angle of 8.90° between the molecular pseudosymmetry plane (Cpcentroid-Ru-C1) and the allenylidene plane (Ru-C1-C2-C3-C4-H3) (Figure 6). This orientation of the allenylidene ligand is consistent with theoretical expectations that  $\pi$ -orbital overlap should be maximized by this geometry.<sup>105-107</sup> The ferrocenyl substituent and cyclopentadienyl ring on ruthenium adopt a *cisoid* conformation, with a Cp<sub>centroid</sub>-Ru-C3-C4 torsion angle of 11.7°. The ferrocenyl C5H4 ring is nearly coplanar with the allenylidene plane, with a (C4-C5-C6-C7-C8)-(Ru-C1-C2-C3-C4-H3) dihedral angle of 13.9°. This orientation maximizes  $\pi$ -orbital overlap between the ferrocenyl C5H4 ring and the attached unsaturated ligand, structurally resembling several ferrocenylstabilized carbocations.<sup>46</sup> The structural characteristics of this

<sup>(103)</sup> Friebolin, H. Basic One- and Two-Dimensional NMR Spectroscopy; VCH: Weinheim, 1993.

<sup>(104)</sup> Gunther, H. *NMR Spectroscopy*; Wiley: New York, 1980; Chapter 6.

<sup>(105)</sup> Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. J. Am. Chem. Soc. 1979, 101, 592–598.

<sup>(106)</sup> Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. J. Am. Chem. Soc. 1979, 101, 585–591.

<sup>(107)</sup> Kostic, N. M.; Fenske, R. F. Organometallics 1982, 1, 974-982.



**Figure 3.** Simulated (upper) and observed (lower) <sup>31</sup>P NMR spectra of complex **2b**.

ligand can be considered in comparison with those obtained for disubstituted complexes  $[Ru(C=C=CPh_2)(PMe_3)_2(Cp)]$ - $[PF_6]$  (8)<sup>31</sup> and  $[Ru(C=C=CPh_2){P(OMe_3)}_2(Cp)][PF_6]$  (9)<sup>108</sup> (Table 4).

The distances of interest differ little among the complexes, despite the difference in basicity of the phosphorus ligands. The Ru1–C1 bonds in complexes **2b**, **8**, **9**, **12**, and **13** are significantly shorter than the Ru–C (sp) bond in  $[Ru(C=CPh)(PPh_3)_2(Cp)]$  (**10**) (2.016(3) Å),<sup>109</sup> but slightly



**Figure 4.** Schematic depicting rotation of the allenylidene ligand with respect to the ruthenium moiety ( $k_{Ru}$ ) and of the ferrocenyl group about the axis of the allenylidene moiety ( $k_{Fe}$ ).



**Figure 5.** ORTEP depiction of the cation (H and solvent atoms omitted for clarity, 20% probability ellipsoids).

longer than most Ru–C (vinylidene) bond lengths (1.83–1.85 Å).<sup>11,31,99</sup> The C1–C2 bond lengths in **2b**, **8**, and **9** are nearly as short as typical carbon–carbon triple bonds, close to that obtained for the C≡C bond in **10** (1.215(4) Å). The C2–C3 lengths are about 0.03 Å longer than a typical allene C(sp)–C(sp<sup>2</sup>) double bond (average 1.307 Å).<sup>110</sup> The geometry of the allenylidene ligand suggests substantial contributions from both allenylidene and propargyl cation resonance forms.<sup>31</sup> The ferrocenyl substituent of complex **2b** apparently does not promote the propargyl form any more than the two phenyl substituents of complexes **8** and **9**. The ferrocenyl to C3 distance in **2b** (C3–C4, 1.429(7) Å) is similar to those previously reported for the ferrocenyl substituents in the complexes [Cr(≡CFc)(Br)-(CO)<sub>4</sub>] (**7b**) (1.40(2) Å)<sup>96</sup> and [W(*E*)-{C(NMe<sub>2</sub>)CH=CH-(Fc)}(CO)<sub>5</sub>] (**11**) (1.63(3), 1.48(2) Å).<sup>111</sup> Since this work

<sup>(108)</sup> Brodsky, R.; McAdoo, E. J.; Selegue, J. P., unpublished results, 1989.

<sup>(109)</sup> Manna, J.; John, K. D.; Hopkins, M. D. Adv. Organomet. Chem. 1995, 38, 78–154.

<sup>(110)</sup> Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. J. Chem. Soc., Perkin Trans. 2 1987, S1–S19.

<sup>(111)</sup> Macomber, D. W.; Madhukar, P.; Rogers, R. D. Organometallics **1989**, 8, 1275–1282.

Table 4. Selected Bond Lengths and Angles for Some Allenylidene Complexes

$[M=C=C=CR^{1}R^{2}]PF_{6}$			bond length (Å)			bond angle (deg)			
[M]	$\mathbf{R}^1$	$\mathbb{R}^2$	Ru-C1	C1-C2	C2-C3	Ru-C1-C2	C1-C2-C3	ref	
$\frac{\text{CpRu}(\text{PPh}_{3})_{2}  2\mathbf{b}}{\text{CpRu}(\text{PMe}_{3})_{2}  8} \\ \text{CpRu}\{\text{P}(\text{OMe})_{3}\}_{2}  9 \\ \text{Cp*Ru}(\text{dippe})  12^{a}$	H Ph Ph H	Fc Ph Ph Ph	1.901(5) 1.884(5) 1.895(7) 1.865(8)	1.258(6) 1.255(8) 1.248(9) 1.25(1)	$ \begin{array}{r} 1.328(7) \\ 1.329(9) \\ 1.344(9) \\ 1.32(1) \end{array} $	172.7(4) 179.5(5) 174.4(6) 172.8(7)	175.1(5) 175.1(7) 166.6(8) 177.5(9)	this work 31 108 61	
RuCl(dppm) <sub>2</sub> 13	Н	Ph	1.89(1)	1.25(1)	1.34(2)	177.0(8)	174(1)	59	

<sup>a</sup> BPh<sub>4</sub> salt.



**Figure 6.** ORTEP depiction highlighting the ferrocenyl substituent. The phenyl groups on the ligands are omitted for clarity (H, phenyl and solvent atoms omitted for clarity, 20% probability ellipsoids).

was completed, there have been a number of complexes structurally characterized that contain the [MC<sub>3</sub>(H)(R)] moiety. The most pertinent are [(Cp\*)Ru(dippe)(C=C= CHPh)][BPh4] (12),<sup>61</sup> [RuCl(dppm)<sub>2</sub>(C=C=CHPh)][PF<sub>6</sub>] (13),<sup>59</sup> and [( $\eta^{5}$ -C<sub>60</sub>Me<sub>5</sub>)Ru(*R*-prophos)(C=C=CHPh)]- $[PF_6]$  (14).<sup>56</sup> The last report is somewhat problematic, as very little information appears in the body of the paper, and on inspection of the CIF file, one finds that the structure contains a second poorly refined molecule in the asymmetric unit, rendering the bond lengths and angles unreliable for comparison. The geometry of the ferrocenyl substituent in 2b is similar to that of 7b and 11. The C-C distances in the substituted cyclopentadienyl ring (C4 to C8,  $\bar{d} = 1.419(8)$  Å) are slightly longer than the C-C distances in the unsubstituted ring (C91 to C95, d = 1.36(1) Å). Although the alternation of C-C bond distances in the substituted cyclopentadienyl ring suggests some contribution of a fulvene resonance form to the structure of 2b, other parameters indicate that this is a very minor contributor. The exo carbon C3 is displaced from the mean cyclopentadienyl plane toward the iron atom by 0.184 Å (Fe-C3, 2.984(7) Å), with the angle  $Cp_{centroid}$ –C4– $C3 = 171.6(5)^{\circ}$  (usually expressed as  $\alpha = 8.4(5)^{\circ}$ ).<sup>46,74–78</sup> For  $[FcCPh_2]^+[BF_4]^-$ , in which the fulvene resonance form is significant, the out-of-plane displacement = 0.50 Å, d(Fe-exo C) = 2.715(6) Å and  $\alpha =$ 20.7°.<sup>74</sup> The ferrocenyl rings of **2b** are nearly parallel, with a (C4-C5-C6-C7-C8) to (C91-C92-C93-C94-C95) dihedral angle of 2.09°, and eclipsed, with torsion angles of opposite carbon atoms ranging from 0.1° to 1.4°, averaging 0.7°.

The triphenylphosphine ligands of **2b** adopt a geometry in which two phenyl rings effectively shield the ferrocenylallenylidene ligand (Figure 6). Several short nonbonding distances are found between the allenylidene chain and the adjacent phenyl rings (C1–C31, 3.200(6) Å; C1–C32, 3.523(6) Å; C2–C32, 3.385(6) Å; C1–C61, 3.396(6) Å; C1–C62, 3.512(6) Å; C2–C62, 3.599(7) Å). This steric shielding probably accounts for the lack of reactivity of compounds **2**–**4** toward nucleophiles. There is a close contact between the allenylidene hydrogen and a  $PF_6^-$  ion (H3–F6, 2.83(5) Å).

**Electrochemistry.** The results of the cyclic voltammetric studies on allenylidene complexes 2b, 3, and 4 are summarized in Table 5, quoted versus internal ferrocene(0/+). The complexes all exhibit similar voltammetric features. Each undergoes a diffusion-controlled, one-electron oxidation, with the separation between anodic and cathodic peak potentials in good agreement with those measured for ferro-cene under identical conditions.<sup>112</sup> This first anodic feature appears to be chemically reversible on the electrochemical time scale if the switching potential remains less than ca. 1000 mV, where  $i_{\rm pc}/i_{\rm pa}$  ratios calculated graphically over the scan range 100 to 1000 mV are unity. At more positive switching potentials, ca. 1800 mV, a second anodic feature is observed with  $E_{\rm pa} \approx 1100$  mV. In the return scan and subsequent scans the chemical reversibility of the first anodic feature is destroyed at scan rates between 100 and 1000 mV with a reduction peak current,  $i_{pc}$ , considerably depressed. When the switching potential is maintained at 1000 mV, an additional feature of interest, at ca. 450 mV, is consistent with adsorption or precipitation of the electroactive species on the electrode surface.<sup>113</sup> A totally irreversible cathodic feature was observed for each complex. Associated with this feature is an anodic return wave (at ca. 0 mV), which is not observed at slow scan rates and is presumably the result of an ECE process.

Clearly, the origin of the anodic wave observed for all the complexes at ca. 300 mV is the ferrocenyl substituent of the allenylidene ligand. The anodic peak potentials observed for this process in complexes **2b**, **3**, and **4** differ by only ca. 70 mV, with the  $E_{1/2}$  values increasing in the order **2b** > **3** > **4** (typically, [Ru(R)(L)<sub>2</sub>(Cp)] (R = alkyl<sup>114,115</sup> or alkynyl<sup>116–119</sup>) complexes

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<sup>(113)</sup> Bard, A. J.; Faulkner, L. R. In *Electrochemical Methods*; Wiley: New York, 1980; pp 488–552.

<sup>(114)</sup> Rogers, W.; Page, J. A.; Baird, M. C. J. Organomet. Chem. 1978, 156, C37-C42.

<sup>(115)</sup> Joseph, M. F.; Page, J. A.; Baird, M. C. *Inorg. Chim. Acta* **1982**, 64, L121–L122.

Table 5. Electrochemical Data for the Allenylidene Complexes

	red <sup>n</sup>	ox <sup>n</sup> 1		ox <sup>n</sup> 2
	$E_{\rm pc}$	$\overline{E_{1/2}\left(\Delta E_{\mathrm{p}} ight)}$	$\sigma_{\rm p}$	$E_{\rm pa}$
2b	-1275	258 (75)	+0.54	1123
3	-1149	313 (120)	+0.67	
4	-1222	324 (74)	+0.69	1068

Scheme 3. Proposed Mechanisms for Oxidation and Reduction of the Allenylidene Complexes

(a) Oxidation



are more difficult to oxidize than the analogous iron complexes by ca. 300 mV). The potential of this ferrocenyl-based redox couple is close to that reported for the related allenylidene complexes  $[TpRu(L)C_3PhFc]$  (L = 2PPh<sub>3</sub>, 360 mV; L = dppf, 370 mV),<sup>53</sup> ca. 30–40 mV lower than that of the chromium carbyne complexes 7, and ca. 15-45 mV higher than that of the tungsten analogues of 7 (Scheme 2).96 The electronic communication between the allenylidene metal headgroup and ferrocenyl moiety is evident in comparison to the related complexes ferrocenyl redox couple is observed at  $E_{1/2}$  20 and 50 mV, respectively, practically unchanged from that of unsubstituted ferrocene. Fischer et al. have used an empirical relationship<sup>120,121</sup> to derive  $\sigma_p$  substituent values from  $E_{1/2}$  data for alkylidyne complexes 7.<sup>96</sup> These  $\sigma_p$  values are probably more reliable than the NMR-based  $\sigma$  values (vide supra). They are generally consistent with the observation that  $[Os(PPh_3)_2(Cp)]^+$  is the least effective  $\pi$ -electron donor of the three iron-group substituents used here, leading to the most carbenium character (propargyl resonance form **B** in Figure 1) and the furthest downfield <sup>1</sup>H NMR shift of H3.

The ferrocenyl-based reversible oxidation gives rise to a dication that slowly precipitates or adsorbs onto the electrode surface, as evinced by an additional feature observable at ca. 450 mV,<sup>113</sup> an effect accelerating with increasing switching potential. The irreversible anodic process at ca. 1100 mV is logically attributed to a Ru<sup>II</sup>/Ru<sup>III</sup> and Os<sup>II</sup>/Os<sup>III</sup> redox couple for **2b** and **4**, respectively,<sup>12</sup> although the lack of

Scheme 4. Products of Reaction after Coupling at  $C\beta$  of Example Alkynyl Complexes<sup>*a*</sup>

$$[M] \equiv C - C \equiv [M] \qquad [M] \equiv C - C = [M]$$
$$[M] \equiv C - C = [M]$$
$$[M] \equiv C - C = [M]$$
$$[M] \equiv C - C = [M]$$

<sup>*a*</sup> tren<sup>#</sup> =  $\kappa^4$ -N,N',N'',N'''-N(CH<sub>2</sub>CH<sub>2</sub>NSiR'<sub>3</sub>)<sub>3</sub>; SiR'<sub>3</sub> = SiMe<sub>3</sub>, SiPhMe<sub>2</sub>.

an observable process for the iron analogue **3** is not readily explained.

We suggest that the irreversibility of the cathodic process may be the result of a ligand-centered coupling of the radicals  $[M(C \equiv CCHFc)(PR_3)_2(Cp)]$  produced by reduction of 2-4 (Scheme 3b). Disubstituted allenylidenes, [Ru(=C=C=CR<sub>2</sub>)- $(dppe)_2Cl]^+$  (R = Me and Ph), have been shown to undergo one-electron reduction to give propargyl radicals that can be trapped by reaction with <sup>n</sup>Bu<sub>3</sub>SnH, giving [Ru(-C=C-CHR<sub>2</sub>)-(dppe)<sub>2</sub>Cl].<sup>122</sup> Subsequently Rigaut and co-workers were able to show an unprecedented coupling of an allenylidene complex with a divnyl complex.<sup>123</sup> Related redox couplings have been reported. Upon reduction and oxidative workup,  $[Cr(C = CPh)(CO)_3(Cp)]$  couples at the  $\beta$ -carbon of the alkynyl ligand, giving neutral complex 15 (Scheme 4).<sup>124</sup> [Mo- $(C = CH) \{N(CH_2CH_2NSiR_3)_3\}$  spontaneously couples at  $C\beta$ to give 16.<sup>125</sup> Oxidation of the anionic vinylidene complex  $[Mo(=C=CHCMe_3){P(OMe)_3}_2(Cp)]^-$  gives the bis-carbyne 17.<sup>126</sup> Several examples of oxidative  $C\beta - C\beta$  couplings of neutral metal alkynyls (or their conjugate acids, vinylidene cations) to give dicationic bis(vinylidene) complexes,<sup>43,117,127,128</sup> as well as  $C\beta$ - $C\beta$  couplings of metal carbene or vinyl complexes,<sup>129,130</sup> have been reported.

## Conclusions

We have demonstrated that the reaction of a ferrocenyl propargylic alcohol has given exceptionally stable monosubstituted allenylidene complexes. The ferrocenyl substituents do not apparently favor either possible resonance form, except perhaps in Os complex **4**, and the stability of the allenylidene complexes almost certainly arises from the steric shielding afforded by the phosphine phenyl substituents. The electrochemical results suggest that these allenylidene complexes are easily oxidized, initially at the ferrocenyl substituent and further oxidized to give an unidentified trication. The most likely reduction product is a propargyl radical that is very reactive. The reactivity of allenylidene complexes is

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clearly dominated by the reaction with nucleophiles at C1 and C3 of the three-carbon chain and with electrophiles at C2. These sites of reactivity are now being developed in methodologies for the formation of carbon-carbon bonds and in alkene metathesis.

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Supporting Information Available: Selected bond lengths and angles for the structure of  $[Ru(C=C=CHFc)(PPh_3)_2(Cp)]$ - $[PF_6] \cdot CH_2Cl_2$ , **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.