# Addition of Alkynes to Coordinated Allyl Ether in **Ruthenium(II)** Chelate Complexes

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Reactions of the ruthenium chelate complex  $[Ru(\eta^5:\eta^2-C_5Me_4CH_2OCH_2CH=CH_2)(CO)Cl]$ (1) with acetylenes  $R^1C \equiv CR^2$  in the presence of AgBF<sub>4</sub> give the cationic diene chelates [Ru- $(\eta^{5}:\eta^{4}-C_{5}Me_{4}CH_{2}OCH_{2}CH=CHCR^{1}=CHR^{2})(CO)]^{+}BF_{4}^{-}$  (**2a**, R<sup>1</sup> = R<sup>2</sup> = Ph; **3a**, R<sup>1</sup> = R<sup>2</sup> = Me; **4a**,  $R^1 = Me$ ,  $R^2 = Ph$ ; **4b**,  $R^1 = Ph$ ,  $R^2 = Me$ ; **5a**,  $R^1 = H$ ,  $R^2 = CO_2Me$ ; **5b**,  $R^1 = CO_2Me$ ,  $R^2$ = H; **6a**,  $R^1$  = H,  $R^2$  = CH<sub>2</sub>OMe) and {Ru[ $\eta^5$ : $\eta^4$ -C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>OCH<sub>2</sub>C(=CH<sub>2</sub>)CH=CHPh](CO)}+- $BF_4^-$  (7). The crystal structures of  $[2a'']^+PF_6^-$  and  $[7]^+PF_6^-$  have been determined. The formation of complexes 2-6 is the result of regiospecific addition of acetylenes PhC=CMe, MeC=CMe, PhC=CMe, HC=CCO<sub>2</sub>Me, and HC=CCH<sub>2</sub>OMe to the terminal carbon of the allylic ether, while phenylacetylene adds to the internal carbon of the olefin. The unsymmetric acetylenes (PhC=CMe, HC=CCO<sub>2</sub>Me) give predominantly the isomers 4a and 5a, where the allylic C–H has added to the acetylenic carbon bearing the less bulky substituent. The complex  $[\operatorname{Ru}(\eta^5:\eta^2-\operatorname{Me}_4C_5CH_2OCH_2CH=CH_2)(\eta^1-C=CPh)(CO)]$  (8) was synthesized by the reaction of **1** with PhC=CLi in THF; the protonation of **8** with  $Et_2O \cdot HBF_4$  gave **7**.

#### Introduction

The ruthenium-catalyzed cross-additions of acetylenes to olefins, leading to the formation of dienes or unsaturated aldehydes and ketones, have recently attracted the attention of several research groups.<sup>1–3</sup> The reason for this strong interest is the high chemoselectivity, which affords organic compounds difficult to make by other methods.<sup>1–4</sup> Monosubstituted olefins and both terminal and internal acetylenes are commonly used as the reagents, and a ruthenacyclopentene mechanism was suggested for the majority of these reactions.<sup>1,2c,3</sup> Participation of vinylidene ruthenium complexes as intermediates has also been discussed in some cases.4b,5

Ruthenium chelate  $\eta^5$ -tetramethylcyclopentadienyl- $\eta^2$ -olefin complexes have recently been synthesized in our laboratories, and their crystal structures and some reactions were published.<sup>6,7</sup> We report here the results of our study of cross-addition of acetylenes to the coordinated olefin in the chelate ruthenium complex  $[\operatorname{Ru}(\eta^{5}:\eta^{2}-\operatorname{C}_{5}\operatorname{Me}_{4}\operatorname{CH}_{2}\operatorname{OCH}_{2}\operatorname{CH}=\operatorname{CH}_{2})(\operatorname{CO})\operatorname{Cl}](\mathbf{1}).$ 

### **Results and Discussion**

The reaction of 1 with AgBF<sub>4</sub> in the presence of acetonitrile leads to substitution of the chloride ligand and formation of the cationic chelate  $[Ru(\eta^5:\eta^2-C_5Me_4-$ CH<sub>2</sub>OCH<sub>2</sub>CH=CH<sub>2</sub>)(CO)(NCMe)]<sup>+</sup>BF<sub>4</sub><sup>-</sup>. <sup>6</sup> When the reaction of 1 with AgBF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> at -30 °C was carried out in the presence of various acetylenes, the cationic  $\eta^5$ -tetramethylcyclopentadienyl- $\eta^4$ -diene chelates **2**-7 were afforded in satisfactory yields (Scheme 1).

The new chelate complexes 2-7 have been characterized by microanalysis and spectroscopically (Tables 1-3), and the structures of  $[2a'']^+PF_6^-$  and  $[7]^+PF_6^$ have been confirmed by single-crystal X-ray diffractometry. All six cations 2-7 exhibit one  $\nu(CO)$  band in the region 2008–2039 cm<sup>-1</sup>, which is at higher frequency than for the neutral chelate **1** [ $\nu$ (CO) 1973 cm<sup>-1</sup>], due to the positive charge. An additional band  $[\nu(CO_2-$ Me) 1725 cm<sup>-1</sup>] is observed for **5a**, **5b**. The NMR resonances arising from the carbonyl groups are observed in the region  $\delta$  197–207 in the <sup>13</sup>C spectra of 2-7. All the methyl and all the ring carbons of the C<sub>5</sub>-Me<sub>4</sub> ligands are inequivalent in both the <sup>1</sup>H and <sup>13</sup>C NMR spectra of 2-7 due to the absence of a plane of symmetry in these complexes. In the <sup>1</sup>H NMR spectra of 2-7 the protons of the  $CH_2-O-CH_2$  fragments are

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BF₄

Scheme 1



2a',a"  $R_1 = R_2 = Ph$ 5a',a"  $R_1 = H, R_2 = CO_2Me$ 3a',a"  $R_1 = R_2 = Me$ 5b  $R_1 = CO_2Me, R_2 = H$ 4a',a"  $R_1 = Me, R_2 = Ph$ 6a',a"  $R_1 = H, R_2 = CH_2OMe$ 4b  $R_1 = Ph, R_2 = Me$ 

Table 1. Yields, v(CO), and Elemental Analysis for<br/>the Complexes 2–8

	IR. $\nu$ (CO) cm <sup>-1</sup>		elemental analysis (%): found (calc)		
complex	(CH <sub>2</sub> Cl <sub>2</sub> )	yield (%)	С	Н	
<b>2</b> <sup>+</sup> (BF <sub>4</sub> <sup>-</sup> )	2012	87	56.54 (57.45)	4.72 (4.99)	
<b>3</b> <sup>+</sup> (BF <sub>4</sub> <sup>-</sup> )	2008	80	46.49 (46.87)	5.03 (5.46)	
$4^{+}(BF_{4}^{-})$	2004	89	52.92 (52.79)	5.98 (5.21)	
$5^{+}(PF_{6}^{-})$	2039, 1725a	15	38.84 (39.35)	4.16 (4.22)	
$6^{+}(PF_{6}^{-})$	2028	30	39.76 (40.38)	4.57 (4.71)	
7 <sup>+</sup> (BF <sub>4</sub> <sup>-</sup> )	2024	91	52.44 (51.88)	5.39 (4.96)	
8	2069, 2098b	69	62.36 (62.31)	5.85 (5.75)	

<sup>*a*</sup>  $\nu$ (COOMe). <sup>*b*</sup>  $\nu$ (C $\equiv$ C).

observed as AX patterns with the expected chemical shifts and coupling constants.<sup>6,7</sup> In the <sup>13</sup>C NMR spectra the  $-O-CH_2$  shows two resonances for each chelate in the region  $\delta$  60–65.

Complexes from Diphenylacetylene. The X-ray structure of chelate 2 shows that it arises from addition of diphenylacetylene to the terminal carbon of the coordinated olefin. In the <sup>1</sup>H and <sup>13</sup>C NMR spectra of 2 two sets of resonances are observed in the ratio 2.6:1.0; we assign these to the conformers 2a' and 2a'' <sup>8a,b,9</sup> (see below). In the <sup>1</sup>H NMR spectrum for both isomers the coordinated diene fragment is characterized by two pairs of doublets at  $\delta$  4.77, 3.56 and 3.33, 4.89, and also by singlets at  $\delta$  4.98 and 3.58, respectively, while in the <sup>13</sup>C NMR the isomers have three tertiary carbon resonances at  $\delta$  60–86 and one signal (due to a quarternary carbon) in the region  $\delta$  90–118 (Table 3). Thus, the NMR data confirm the presence of the CH=CH-CPh= CHPh moiety in both isomers. It should be noted that similar isomers are observed for all the other cations 3a-6a.

**Complexes from 2-Butyne.** 2-Butyne also adds to the terminal carbon of the olefin to give the diene chelate  $[\text{Ru}(\eta^5:\eta^4\text{-}C_5\text{Me}_4\text{CH}_2\text{OCH}_2\text{CH}=\text{CHCMe}=\text{CHMe})$ - $(\text{CO})]^+\text{BF}_4^-$  (**3a**'). The incorporation of 2-butyne results in the appearance of two more methyl resonances in the <sup>1</sup>H and <sup>13</sup>C NMR spectra of **3a**' than are found in **1**. Two doublets at  $\delta$  3.11 and 5.02 confirm the presence of a -CH=CH- moiety, while the doublet at  $\delta$  1.83 (J=6.3Hz) and the quartet at  $\delta$  3.90 (J=6.3 Hz) arise from a =CHMe group. In the <sup>13</sup>C NMR spectrum three resonances due to tertiary carbons at  $\delta$  71–85 and one resonance due to a quarternary carbon at  $\delta$  88–118 (Table 3) are observed in accordance with the suggested structure of **3**. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **3a**' also show an additional set of Me group signals that presumably belong to the second isomer **3a**'', present to the extent of  $\leq 10\%$ .

Complexes from Phenylpropyne. Reaction of the unsymmetric phenylpropyne with 1 gives a mixture of three isomeric chelates [ $Ru(\eta^5:\eta^4-C_5Me_4CH_2OCH_2CH=$ CHCMe=CHPh)(CO)]+BF<sub>4</sub>- (4a', 4a'') and [Ru( $\eta^5$ : $\eta^4$ -C<sub>5</sub>- $Me_4CH_2OCH_2CH=CHCPh=CHMe)(CO)]^+BF_4^-$  (4b) in the ratio 4a':4a'':4b = 1.8:1.0:1.5. The NMR spectra show that here again the addition of the acetylene occurs exclusively to the terminal carbon of the olefin for all three complexes 4a', 4a", and 4b. Thus three pairs of doublets at  $\delta$  3.19 and 5.11, 2.94 and 4.48, and 3.31 and 4.59, arising from –CH=CH– moieties, are observed in the <sup>1</sup>H NMR spectrum of **4a**', **4a**", and **4b**. In the <sup>13</sup>C NMR spectrum the signals of three tertiary carbons and one quarternary carbon are found for each of three isomers 4a', 4a", and 4b, due to the -CH=  $CH-CMe{Ph}=CHPh{Me}$  moiety. In the <sup>1</sup>H NMR spectrum the =CHPh groups of isomers 4a', 4a" show two singlets at  $\delta$  4.50 and 3.31, while **4b** shows a doublet at  $\delta$  2.24 (J = 7.0 Hz) and a quartet at  $\delta$  4.00 (J = 7.0 Hz), corresponding to the =CHMe group. This is evidence that the terminal carbon of the olefin can attack at the carbon of the acetylene bearing either the methyl or the phenyl substituents to afford 4a' + 4a'' or 4b, respectively. Addition to the carbon carrying the less bulky substituent is more preferred, and the overall ratio of (4a' + 4a''):4b is 1.9:1.0.

Complexes from Methyl Propiolate. Methyl propiolate, a monosubstituted acetylene, reacts with 1 similarly to phenylpropyne, with the terminal carbon of the coordinated olefin adding to both the substituted carbon and the unsubstituted carbon of the acetylene to give a mixture of the three isomers  $[Ru(\eta^5:\eta^4-C_5Me_4 CH_2OCH_2CH=CHCH=CHCO_2Me)(CO)]^+BF_4^-$  (5a', 5a'') and { $Ru[\eta^5:\eta^4-C_5Me_4CH_2OCH_2CH=CH-C(CO_2Me)=$  $CH_2](CO)$ <sup>+</sup>BF<sub>4</sub><sup>-</sup> (**5b**) in the ratio **5a**':**5a**'':**5b** = 1.0:4.7: 2.1. The ester  $CO_2Me$  groups of the isomers **5a**', **5a**'', and **5b** show three singlets at  $\delta$  3.79, 3.78, and 4.01 in the <sup>1</sup>H NMR spectrum and at  $\delta$  168.0, 53.4; 168.4, 57.0; and 164.7, 55.7 in the <sup>13</sup>C NMR spectrum, respectively. The presence of the diene fragments -CH=CH-CH= CHCO<sub>2</sub>Me of isomers **5a**', **5a**" is indicated by four pairs of multiplets at  $\delta$  3.1–6.3 in the <sup>1</sup>H NMR spectrum and by four pairs of tertiary carbons at  $\delta$  62–95 in the <sup>13</sup>C NMR spectrum. The diene moiety -CH=CH-

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Table 2. <sup>1</sup>H NMR Data for Ruthenium Chelates  $[Ru(\eta^5:\eta^4-C_5Me_4CH_2OCH_2CH=CHCR^1=CHR^2)(CO)]^+ (\delta)^a$ 

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$\mathbb{N}_{2}, \mathbb{R}^{1}, \mathbb{R}^{2}$	C5Me4	CH <sub>2</sub> O	OCH <sub>2</sub>	-CH=	=CH-	R <sup>1</sup>	CHR <sup>2</sup>
2a'	1.72; 1.78;	3.52 (d, J = 14.4);	3.15 (dd, J = 15.5, 3.8);	4.77 (ddd,	3.56 (d,	7.0 - 7.4 m	4.98 s; 7.0 - 7.4 (m, Ph)
$R^1 = R^2 = Ph$	2.19; 2.29	4.59 (d, J = 14.4)	4.36 (dd, J = 15.5, 2.0)	J = 11.1, 3.8, 2.0)	J = 11.1)		
2a''	1.25; 1.42;	3.57 (d, J = 14.2);	3.13 (dd, J = 15.5, 2.5);	3.33 (ddd,	4.89 (d,	7.0 - 7.4 m	3.58 s; 7.0 - 7.4 (m, Ph)
$\mathbf{R}^1 = \mathbf{R}^2 = \mathbf{P}\mathbf{h}$	2.28; 2.31	4.63 (d, J = 14.2)	4.42 (dd, J = 15.5, 1.0)	J = 9.0, 2.5, 1.0)	J = 9.0)		
3a'	<sup>b</sup> 1.60; 1.89;	3.44 (d, J = 14.2);	3.15 (dd, J = 15.7, 3.7);	5.02 (ddd,	3.11 (d,		1.83 (d, Me, $J = 6.3$ );
$R^1 = R^2 = Me$	2.15°; 2.18	4.49 (d, J = 14.2)	4.26 (dd, J = 15.7, 1.7)	J = 11.1, 3.7, 1.7)	J = 11.1)		3.90 (q, J = 6.3)
4a'	<sup>b</sup> 1.62; 1.69;	3.48 (d, J = 14.0);	3.00 (dd, J = 15.6, 4.0);	5.11 (ddd,	3.19 (d,		4.50 s, 7.0 - 7.5 (m, Ph)
$R^1 = Me;$ $R^2 = Ph$	2.00; 2.09; 2.20	4.57 (d, J = 14.0)	4.35 (dd, J = 15.6, 2.4)	J = 10.9, 4.0, 2.4)	J = 10.9)		
4a''	<sup>b</sup> 1.89; 1.94;	3.46 (d, J = 14.4);	2.9 – 3.1 m;	2.94 (ddd,	4.48 (d,		3.31 s; 7.0 - 7.5 (m, Ph)
$R^1 = Me;$	2.02; 2.07;	4.70 (d, J = 14.4)	4.3 – 4.5 m	J = 9.0, 2.4, 1.6)	J = 9.0)		
$R^2 = Ph$	2.11						
4b	1.73; 2.01;	3.49 (d, J = 14.6);	3.17 (dd, J = 15.6, 4.0);	4.59 (ddd,	3.31 (d,	7.0 - 7.5 m	2.24 (d, Me, J = 7.0);
$R^1 = Ph; R^2 = Me$	2.26; 2.28	4.59 (d, J = 14.6)	4.40 (dd, J = 15.6, 2.4)	J = 10.9, 4.0, 2.4)	J = 10.9)		4.00 (q, J = 7.0)
<sup>d</sup> 5a'	1.76; 2.29;	3.60 (d, J = 14.4);	3.29 (dd, J = 15.7, 3.7);	5.39 (ddd,	3.74 (dd, J =	5.24 (dd,	3.79 (s, Me)
$R^1 = H; R^2 = CO_2Me$	2.30; 2.33	4.69 (d, J = 14.4)	4.37 (dd, J = 15.7, 1.0)	J = 10.9, 3.7, 1.0)	10.9, 8.2)	J =11.3, 8.2)	4.03 (d, J = 11.3)
<sup>d</sup> 5a''	1.78; 2.11;	3.73 (d, J = 14.5);	3.25 (dd, J = 15.9, 2.7);	3.76 (ddd,	4.92 (dd, J =	6.22 (dd,	3.78 (s, Me)
$R^1 = H; R^2 = CO_2Me$	2.18; 2.43	4.78 (d, J = 14.5)	4.38 (dd, J = 15.9, 1.2)	J = 9.4, 2.7, 1.2)	9.4, 6.8)	J = 9.8, 6.8)	3.17 (d, J = 9.8)
<sup>d</sup> 5b	1.59; 1.87;	3.72 (d, J = 14.5);	3.20 (dd, J = 15.7, 2.9);	3.42 (ddd,	5.29 (d,	4.01 (s, Me)	2.48 (d, J = 2.0)
$R^1 = CO_2Me; R^2 = H$	2.27; 2.44	4.76 (d, J = 14.5)	4.36 (dd, J = 15.7, 1.4)	J = 9.5, 2.9, 1.4)	J = 9.5)		4.65 (d, J = 2.0)
6a'	1.71; 2.24;	3.61 (d, J = 14.3);	3.22 (dd, J = 15.8, 3.6);	4.61 (ddd,	3.41 (dd, J =	4.50 (dd,	4.37 (ddd, J=11.8; 4.2, 3.2);
$R^1 = H;$	2.28; 2.30	4.66 (d, J = 14.3)	4.28 (dd, J = 15.8, 1.0)	J = 10.8, 3.6, 1.0)	10.8, 8.0)	J = 11.8, 8.0)	3.38 (s, 3H, OMe); 3.80 (dd,
$R^2 = CH_2OMe$							(dd, CHHOMe, J = 14.1, 4.2); 4.08 (dd, CHHOMe, J = 14.1, 3.2)
6a''	1.93; 2.06;	3.69 (d, J = 14.4);	3.15 (dd, J = 15.5, 2.7);	3.36 (ddd,	4.64 (dd, J =	5.80 (dd,	3.30 (ddd, J=10.3, 5.6, 4.8);
$\mathbf{R}^{1} = \mathbf{H};$	2.25; 2.38	4.75 (d, J = 14.4)	4.28 (dd, J = 15.5, 1.0)	J = 9.0, 2.7, 1.0)	9.0, 6.8)	J = 10.3, 6.8)	3.41 (s, 3H, OMe); 3.82 (dd,
$R^2 = CH_2OMe$		. ,					(dd, CHHOMe, J = 12.6, 5.6); 3.90 (dd, CHHOMe, J = 12.6, 4.8)

<sup>*a*</sup> All spectra obtained in CDCl<sub>3</sub> at 300K, J in Hz. <sup>*b*</sup> One singlet arising from  $R^1 = Me$ . <sup>*c*</sup>6H, 2Me. <sup>*d*</sup>In (CD<sub>3</sub>)<sub>2</sub>CO.

$R^1, R^2$	C <sub>5</sub> Me <sub>4</sub>	C <sub>5</sub> Me <sub>4</sub>	CH <sub>2</sub> OCH <sub>2</sub>	-СН=СН-С=СН	со	R <sup>1</sup> , R <sup>2</sup>
$2a' R^1 = R^2 = Ph$	7.2; 10.6; 10.7; 10.8	<sup>b</sup> 94.3; 98.2; 99.1; 99.2; 117.3; 118.8	60.7; 63.9	° 73.9; 77.9; 85.9	199.9	127.9 (CH); 128.1 (CH); 128.3 (CH);128.5 (CH); 129.3 (CH);130.2 (CH); 130.5 (CH); 130.9 (C); 134.5 (C)
$2a''$ $R^1 = R^2 = Ph$	7.7; 8.4; 10.3; 14.8	<sup>b</sup> 90.2; 99.7; 101.2; 102.8; 110.4; 111.2	61.5; 64.6	° 60.1; 78.8; 79.7	204.5	127.8 (CH); 127.9 (CH); 128.3 (CH); 129.9 (CH); 130.0 (CH); 130.2 (CH); 130.5 (CH); 131.2 (C); 134.5 (C)
$3a'  R^1 = R^2 = Me$	<sup>d</sup> 7.0; 9.8; 9.9; 10.0; 14.0; 15.0	<sup>b</sup> 93.0; 98.0; 98.3; 98.9; 113.0; 115.3	60.6; 64.0	° 71.3; 80.4; 84.1	199.1	
<b>4a'</b> $R^1 = Me; R^2 = Ph$	°6.9; 9.3; 9.5; 10.1; 14.2;	<sup>b</sup> 88.5; 98.8; 99.7; 100.0; 112.0; 117.3	60.8; 64.1	° 73.5; 75.2; 84.0	201.2	128.4 (CH); 129.4 (CH); 130.8 (CH); 131.9 (C)
<b>4a''</b> $R^1 = Me; R^2 = Ph$	*8.0; 8.8; 9.5; 10.0; 16.8	<sup>b</sup> 90.0; 99.2; 101.8; 103.8; 106.3; 117.6	61.6; 64.6	° 73.6; 79.2; 84.0	206.5	128.6 (CH); 128.8 (CH); 139.1 (CH); 132.1 (C)
<b>4b</b> $R^{1} = Ph; R^{2} = Me$	°6.9; 9.4; 9.6; 10.1; 15.1	<sup>b</sup> 94.2; 94.3; 98.6; 99.1; 110.9; 118.4;	61.0; 64.2	° 79.4; 81.5; 83.7	201.5	128.3 (CH); 129.0 (CH); 129.8 (CH); 130.4 (C)
$^{f}$ 5a' R <sup>1</sup> = H; R <sup>2</sup> = COOMe	7.4; 9.6; 9.9; 10.5	94.5; 100.8; 102.0; 105.8; 121.0	60.5; 63.7	69.1; 76.5; 79.6; 85.2	197.6	53.4 (OMe); 168.0 (COO)
${}^{f}5a''$ R <sup>1</sup> = H; R <sup>2</sup> = COOMe	7.8; 9.4; 9.6; 10.1	88.2; 100.4; 105.2; 106.1; 110.6	61.8; 64.5	62.2; 64.7; 88.1; 94.5	204.3	57.0 (OMe); 168.4 (COO)
<sup>f</sup> <b>5b</b> $R^1 = COOMe; R^2 = H$	7.4; 9.4; 9.9; 10.1	<sup>b</sup> 94.5; 95.9; 99.1; 99.7; 100.2; 104.7	61.7; 64.7	° 52.4; 85.2; 91.5	204.4	55.7 (OMe); 164.7 (COO)
<b>6a'</b> $R^1 = H; R^2 = CH_2OMe$	7.7; 10.1; 10.3; 10.5	92.9; 98.0; 98.3; 99.3; 117.7	60.8; 63.8	71.2; 77.4; 90.3; 92.2	197.8	58.8 (OMe); 69.7 (CH <sub>2</sub> )
6a'' R <sup>1</sup> = H; R <sup>2</sup> = CH <sub>2</sub> OMe	9.4; 9.8; 10.2; 10.4	90.6; 98.9; 101.6; 102.8; 110.0	62.0; 64.9	59.5; 77.7; 84.5; 91.3	204.8	58.9 (OMe); 71.0 (CH <sub>2</sub> )

<sup>*a*</sup> All spectra obtained in CDCl<sub>3</sub> at 300K, *J* in Hz. <sup>*b*</sup> Five quanternary carbons arise from Cp<sup>\*</sup> ring, and one arises from diene moiety. <sup>*c*</sup> Three resonances arise from tertiary carbons of diene moiety. <sup>*d*</sup> Four resonances arise from Cp<sup>\*</sup> methyls, and two arise from acetylenic methyls; two resonances are overlapped. <sup>*e*</sup> Four resonances arise from Cp<sup>\*</sup> methyls, and one arises from acetylenic methyl. <sup>*f*</sup> In (CD<sub>3</sub>)<sub>2</sub>CO.

C(CO<sub>2</sub>Me)=CH<sub>2</sub> of isomer **5b** shows four proton signals at  $\delta$  2.48, 3.42, 4.65, and 5.29 in the <sup>1</sup>H NMR spectrum, and signals due to one secondary carbon at  $\delta$  52.4, two tertiary carbons at  $\delta$  85.2, 91.5, and one quarternary carbon at  $\delta$  95–105 in the <sup>13</sup>C NMR spectrum. The protons of one of the methylene groups of the CH<sub>2</sub>OCH<sub>2</sub> moiety in **5b** at  $\delta$  3.20 and 4.36 show vicinal coupling constants J = 2.9 Hz and J = 1.4 Hz along with  $J_{AB} = 15.7$  Hz due to their interaction with the vinyl proton of the diene moiety ( $-O-CH_2-CH=$ ), which is typical for all complexes **2–6** and confirms the proposed structure. The alternative diene structure,  $-C(= CH_2)CH=CHCO_2Me$ , formed as a result of addition of methyl propiolate to the internal carbon of the olefin,





can be ruled out since there the bridged methylene group is linked to the quarternary carbon of the diene moiety and only one constant  $J_{AB} = \sim 16$  Hz should be observed.

Complexes from Methyl Propargyl Ether. Addition of methyl propargyl ether to 1 occurs regiospecifically so that the terminal carbon of the olefin links only to the unsubstituted carbon of the acetylene, unlike the situation for phenylpropyne and methyl propiolate. This gives a mixture of isomers indentified as  $[Ru(\eta^5:\eta^4-C_5 Me_4CH_2OCH_2CH=CHCH=CHCH_2OMe)(CO)]^+BF_4^-$  (6a', 6a''), in the ratio 6a':6a'' = 1.0:1.7, from their NMR spectra. In the <sup>1</sup>H and <sup>13</sup>C NMR spectra of **6a'**, **6a**" the signals of the MeO groups are observed at  $\delta$  3.38, 3.41 and 58.8, 58.9, respectively. Resonances arising from the methylene group of CH<sub>2</sub>OMe moiety are found in the region  $\delta$  3.8–4.1 and at 69.7 (**6a**') and 71.0 (**6a**''). In the <sup>13</sup>C NMR spectrum the diene fragment -CH=CH-CH= CHCH<sub>2</sub>OMe shows two sets of tertiary carbons at  $\delta$  71.2, 77.4, 90.3, 92.2 (6a') and 59.5, 77.7, 84.5, 91.3 (6a'').

Complexes from Phenylacetylene. The reaction of 1 with phenylacetylene unexpectedly gave the diene chelate { $Ru[\eta^5:\eta^4-C_5Me_4CH_2OCH_2C(=CH_2)CH=CHPh]$ -(CO)}<sup>+</sup>BF<sub>4</sub><sup>-</sup> (7), wherein the unsubstituted carbon of the acetylene is linked to the internal carbon of the coordinated olefin. The structure of 7 was determined by single-crystal X-ray diffractometry. Complex 7 exists in solution as a single isomer. In the <sup>1</sup>H NMR spectrum the diene fragment  $-C(=CH_2)-CH=CHPh$  shows two pairs of doublets at  $\delta$  3.83 (*J* = 11.2 Hz), 5.68 (*J* = 11.2 Hz) and 2.06 (J = 2.9 Hz), 3.07 (J = 2.9 Hz). The signals of the methylene group protons of the -CH<sub>2</sub>OCH<sub>2</sub>moiety, which are bound to the quaternary carbon of the diene, appear as two doublets ( $J_{AB} = 14.7$  Hz), with no other coupling observed; this is in contrast to the analogous signals for complexes 2-6. The <sup>13</sup>C NMR spectrum of **7** shows signals at  $\delta$  47.8 (CH<sub>2</sub>), 75.9 (CH), 82.5 (CH) and the quarternary carbon in the region 94-106 arising from the diene fragment.

Synthesis and Protonation of  $[\mathbf{Ru}(\eta^5:\eta^2-\mathbf{Me}_4\mathbf{C}_5-\mathbf{CH}_2\mathbf{OCH}_2\mathbf{CH}=\mathbf{CH}_2)(\eta^1-\mathbf{C}=\mathbf{CPh})(\mathbf{CO})]$  (8). Nucleophilic substitution occurred at the ruthenium center when complex 1 was reacted with LiC=CPh in THF at -78 °C; this led to the  $\sigma$ -acetylide complex 8 in 69% yield (Scheme 2).

Complex **8** was characterized spectroscopically. In the IR spectrum  $\nu$ (CO) at 2069 cm<sup>-1</sup> and  $\nu$ (C=C) at 2098 cm<sup>-1</sup> are observed. In the <sup>1</sup>H and <sup>13</sup>C NMR spectra the four methyl signals of the C<sub>5</sub>Me<sub>4</sub> ring are found. The <sup>1</sup>H NMR spectrum shows two doublets at  $\delta$  3.33, 4.06 (J = 13.0 Hz) and two doublets of doublets at  $\delta$  3.05, 4.22 (J = 15.0 Hz, J = 2.0 Hz) arising from the CH<sub>2</sub>-OCH<sub>2</sub> moiety. The presence of the phenyl is shown by a multiplet at  $\delta$  7.1–7.8 in the <sup>1</sup>H NMR spectrum and

by the resonances of three tertiary carbons at  $\delta$  124.8, 128.2, 131.7 and one quaternary carbon at  $\delta$  130.2 in the <sup>13</sup>C NMR spectrum. The signals of two acetylenic carbons appear in the region  $\delta$  90–110 together with five quarternary carbons of the C<sub>5</sub>Me<sub>4</sub> ring.

The signals of the  $-CH=CH_2$  moiety are observed at  $\delta$  2.04, 2.84, 4.06 and at  $\delta$  39.5, 68.0 in the <sup>1</sup>H and <sup>13</sup>C NMR spectra, respectively. The spectral data show that the complex **8** is only one isomer in solution. The reasons that only one diastereomer of **8** has been obtained in more than 50% yield from two equally populated diastereomers of **1**<sup>6</sup> are not clear. It should be noted that the reaction of **1** with KX (X = Br, I) led to formation of a mixture of diastereomers [Ru( $\eta^5:\eta^2$ -Me<sub>4</sub>C<sub>5</sub>CH<sub>2</sub>OCH<sub>2</sub>-CH=CH<sub>2</sub>)(CO)X].<sup>6</sup>

 $\sigma$ -Acetylide ruthenium complexes usually undergo protonation to vinylidene compounds.<sup>10a,b</sup> However, protonation of **8** by Et<sub>2</sub>O·HBF<sub>4</sub> does not stop at vinylidene complex formation, but addition of the vinylidene to the coordinated olefin occurs, yielding the previously described diene chelate **7** as the final product (Scheme 3).

Crystal Structures of the [Ru{ $\eta^2:\eta^5-C_5Me_4CH_2OC-H_2CH=CH-CPh=CHPh$ }CO]<sup>+</sup> (2a''<sup>+</sup>) and [Ru{ $\eta^2:$  $\eta^5-C_5Me_4CH_2OCH_2(CH_2=)C-CH=CHPh$ }CO]<sup>+</sup> (7<sup>+</sup>). X-ray structure determinations have been carried out on [Ru{ $\eta^5:\eta^4-C_5Me_4CH_2OCH_2CH=CH-CPh=CHPh$ }-CO]<sup>+</sup>PF<sub>6</sub><sup>-</sup> and on [Ru{ $\eta^2:\eta^5-C_5Me_4CH_2OCH_2(CH_2=)C-CH=CHPh$ }CO]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (Figures 1, 2), prepared by additionofNH<sub>4</sub>PF<sub>6</sub> to aqueous solutions of the tetrafluoroborate salts of [2a'']<sup>+</sup> and [7]<sup>+</sup>, respectively. Representations of the structures found for the cations of 2a'' and 7 with the atomic numbering schemes are presented in Figures 1 and 2, and the selected bond lengths and bond angles are given in Table 4.

In both structures the ruthenium atom is coordinated by the tetramethylcyclopentadienyl ligand, the carbonyl group, and the terminal diene moiety of the pendant chain of the substituted cyclopentadienyl ring. It should be noted that in complex 7 the diene moiety is linked to the pendant chain by the internal diene atom (C(13)), while in complex 2a'' it is linked to the terminal atom (C(12)).

The main differences in the geometry of these two complexes are found in the diene fragment. In complex 7 the  $CH_2 = C(CH_2) - CH = CHPh$  diene moiety has an *s-cis*-conformation (Figure 1, 3a), while in **2a**" the (CH<sub>2</sub>)-CH=CH-CPh=CHPh fragment is characterized by an s-trans-conformation (Figures 2, 3b). The torsion angles C(12)C(13)C(14)C(15) are 125.5° and -2.5° in **2a**" and 7, respectively. Analogous torsion angles in the unchelated diene complexes are about 122°. <sup>8a,b,9</sup> Our data suggest that the double bonds are more localized in the *s-cis*-diene in **7** than in the *s-trans*-diene in complex **2a**<sup>"</sup>. For 7 we find two equal bonds C(14)-C(15) and C(12)-C(15)C(13) of length 1.38(1) Å and one bond C(13)-C(14) of length 1.47(1) Å, while in complex 2a" the corresponding bond lengths seem more similar (1.40(1), 1.43(1), and 1.47(1) Å, respectively). The  $Ru-C_{diene}$  bond lengths vary from 2.150(8) to 2.311(8) Å in **2a**" and 2.202(7) to 2.359(7) Å in cation 7, with the longer distance in both structures to the terminal carbon C(15). In structure 7,

<sup>(10) (</sup>a) Bruce, M. I. Chem. Rev. **1991**, *91*, 197. (b) Davies, S. G.; McNally, J. P.; Smallridge, A. J. Adv. Organomet. Chem. **1990**, *30*, 1.

**Scheme 3** 







**Figure 1.** General view of complex **7** and atomic numbering. Thermal ellipsoids are drawn at the 50% probability level. The  $PF_6^-$  anion is omitted for clarity.



**Figure 2.** General view of complex **2a**" and atomic numbering. Thermal ellipsoids are drawn at the 50% probability level. The  $PF_6^-$  anion is omitted for clarity. the phenyl ring is approximately coplanar with the diene fragment (C(14)C(15)C(16)C(17) torsion angle is 172.5°). In complex **2a**" two Ph rings have different orientations with respect to the diene fragment, with torsion angles C(13)C(14)C(16)C(17) and C(14)C(15)C-(22)C(23) equal to  $-31.1^\circ$  and  $-92.2^\circ$ , respectively.

The six-membered metallacycles in 2a" (RuC(1)C(6)O-



Table 4. Selected Bond Lengths (Å) and Angles (deg) in the Structures 2a" and 7

$C_{28}H_{29}O_2RuPF_6$ (2a'')		C <sub>22</sub> H <sub>25</sub> O <sub>2</sub> RuPF <sub>6</sub> (7)				
Bond Lengths						
Ru-C(1)	2.199(8)	Ru - C(1)	2.181(7)			
Ru-C(2)	2.252(7)	Ru-C(2)	2.227(7)			
Ru-C(3)	2.277(8)	Ru-C(3)	2.207(6)			
Ru-C(4)	2.211(9)	Ru-C(4)	2.211(6)			
Ru-C(5)	2.187(8)	Ru-C(5)	2.202(7)			
Ru-C(12)	2.288(9)	Ru-C(12)	2.236(9)			
Ru-C(13)	2.150(9)	Ru-C(13)	2.169(7)			
Ru-C(14)	2.253(8)	Ru-C(14)	2.202(7)			
Ru-C(15)	2.311(8)	Ru-C(15)	2.359(7)			
Ru-C(28)	1.886(7)	Ru-C(22)	1.914(8)			
O(1)-C(6)	1.42(1)	O(1)-C(11)	1.44(2)			
O(1)-C(11)	1.45(1)	O(1)-C(6)	1.44(1)			
O(2)-C(28)	1.155(9)	O(2)-C(22)	1.13(1)			
C(1)-C(6)	1.50(1)	C(1)-C(6)	1.51(1)			
C(11)-C(12)	1.51(1)	C(11)-C(13)	1.50(1)			
C(12)-C(13)	1.40(1)	C(12)-C(13)	1.38(1)			
C(13)-C(14)	1.47(1)	C(13)-C(14)	1.47(1)			
C(14)-C(15)	1.43(1)	C(14)-C(15)	1.38(1)			
	Bond	Angles				
C(12)-Ru-C(15)	99.5(3)	C(12) - Ru - C(15)	76.8(3)			
C(13)-Ru-C(14)	38.9(3)	C(13)-Ru-C(14)	39.2(3)			
C(13)-Ru-C(12)	36.7(3)	C(13)-Ru-C(12)	36.4(4)			
C(13)-Ru-C(15)	65.3(3)	C(13) - Ru - C(15)	66.3(3)			
C(14)-Ru-C(12)	65.5(3)	C(14) - Ru - C(12)	67.2(4)			
C(14)-Ru-C(15)	36.5(3)	C(14) - Ru - C(15)	35.1(3)			
C(6) - O(1) - C(11)	113.6(7)	C(6) - O(1) - C(11)	111.5(9)			
O(1) - C(6) - C(1)	113.8(7)	O(1) - C(6) - C(1)	114.0(8)			
O(1) - C(11) - C(12)	113.5(7)	O(1) - C(11) - C(13)	114.1(9)			
C(13)-C(12)-C(11)	121.7(8)	C(12)-C(13)-C(14)	119.4(9)			
C(12)-C(13)-C(14)	117.6(8)	C(12)-C(13)-C(11)	122.2(9)			
C(13) - C(14) - C(16)	120.7(7)	C(14) - C(13) - C(11)	118.1(10)			
C(15)-C(14)-C(13)	112.6(7)	C(15)-C(14)-C(13)	121.1(10)			
C(15)-C(14)-C(16)	126.6(7)	C(14) - C(15) - C(16)	123.7(8)			
C(14) - C(15) - C(22)	124.9(7)	O(2)-C(22)-Ru	175.4(8)			
O(2)-C(28)-Ru	172.8(7)					

(1)C(11)C(12)) and **7** (RuC(13)C(11)O(1)C(6)C(1)) are characterized by the sofa conformation with the O(1) atom deviating by 0.72 Å. In both structures the oxygen atom of the pendant chain is oriented away from the CO group (Figure 3a,b).

Analysis of the molecular packing reveals that the crystal structures **2** and **7** consist of the discrete cations and anions with no abnormally close intermolecular contacts.

**The Isomerism of Complexes 2a–6a.** According to the <sup>1</sup>H NMR data the complexes **2a–6a** exist in solution as pairs of isomers **2a'–6a'** and **2a''**, **4a''–6a''**, which are not the regioisomers. It has previously been shown that acetylacetonate ruthenium(II) complexes [Ru( $\eta^4$ diene)(acac)<sub>2</sub>] tend to complex dienes *s*-*trans*,<sup>8a,b</sup> while pentamethylcyclopentadienylruthenium(II) complexes tend to complex them *s*-*cis*.<sup>9</sup> The X-ray structure for **2a** 



**Figure 3.** Projections of the cations **7** (a) and **2a**" (b) to the plane of the cyclopentadienyl ring. The Ph groups are omitted for clarity.

shows an *s*-*trans* diene conformation in the solid. Complexes **2a**–**6a** are thus proposed to exist in solution either as mixtures of *s*-*trans* and *s*-*cis* isomers or two different *s*-*trans* isomers, analogous to those found in the acetylacetonate ruthenium complexes.<sup>8a,b</sup> The isomerism of complexes **2a**–**6a** can be explained not only in terms of isomerism of the diene but also because of the other reasons. For instance the presence of the isomers could be stipulated by *Z*/*E*-isomerism of substituents at the double bonds or by CH<sub>2</sub>–O–CH<sub>2</sub> moiety conformerism (Scheme 4). *Z*/*E*-isomerism of the substituents could not be realized because of the specificity of diene chelate formation (see below).

Interconversion of 2a'-6a' and 2a'', 4a''-6a'' isomers could be an argument for denying Z/E-isomerism for these complexes. Attempts to carry out NMR experiments at temperatures high enough to coalesce any resonances that were exchanging failed due to decomposition under these conditions. Therefore a 2D <sup>1</sup>H EXSY NMR experiment was carried out on 2a at 300 K in acetone- $d_6$  (Figure 4), and this revealed the exchange of complex 2a' protons with the corresponding protons of **2a**". The approximate energy of activation  $\Delta G^{\ddagger}$  value for the interconversion **2a**'  $\rightarrow$  **2a**" is about 18 kcal/mol. Thus, the isomerism of **2a**' and **2a**" is not caused by the different configuration of the substituents in the olefin fragments. Both complexes are the products of *cis*addition of an allylic C–H bond to acetylene. Acetylene adds to the coordinated olefin *trans* to the chelate bridge.

Another possible reason for isomerism in complexes 2a-6a could be because the oxygen of the  $CH_2-O-CH_2$  fragment can be directed toward the carbonyl group or away from it (Scheme 5).

However it is doubtful that such conformers could be seen in solution. The oxygen in this fragment would not be coordinated, and as a consequence, the activation energy of such an interconversion should be comparable with that in organic cyclic oxygen containing compounds with a similar ring size. The  $\Delta G^{\ddagger}$  is usually low ( $\approx 9-12$  kcal/mol), and the average signals are observed at room temperature in NMR spectra of such compounds.

Therefore, the most probable isomerism type of complexes 2a-6a is conformerism of the diene moiety. The diene fragment can have either *s*-*cis*- or *s*-*trans*conformation, and there are two states of *s*-*trans*conformation: when the H<sub>a</sub> proton is oriented to a metal atom (*s*-*trans*-isomer **II**) and away from it (*s*-*trans*isomer **I**), as shown in Scheme 6.

**Mechanistic Considerations.** The following regularities have been revealed for the cross-addition reactions of acetylenes to the coordinated olefin in the chelate complex 1: (1) the formation of coordinated 1,3-dienes takes place in all cases; (2) the addition to the coordinated olefin occurs regiospecifically either to terminal carbon (complexes 2-6) or to the internal carbon (complex 7); (3) in unsymmetric acetylenes the carbon bearing the less bulky substituent is favored to add to the olefin.

Previous studies of the *catalytic* cross-addition of acetylenes to olefins have been shown to proceed via a ruthenacyclopentene<sup>1,2c,3</sup> or through a vinylidene mechanism.<sup>4b,5</sup> The regularities found for the formation of 2-6 can be satisfactorily explained by a metallacyclopentene mechanism, as outlined in Scheme 7.

The catalytic reactions with nonchelate ruthenium complexes usually lead to the formation of 1,4-dienes.<sup>1,2c,3</sup> In the stoichiometric reactions discussed here formation of a 1,4-diene in the chelate complex would lead to a highly strained structure, which would have only two bridging atoms,  $-CH_2-O-$ . The formation of a 1,4-diene would also be prohibited because of the impossibility of  $\beta$ -elimination from the methylene group bound to the oxygen, which is in a rigid chelate cycle and distant from the ruthenium center.

The reaction of **1** with phenylacetylene in the presence of AgBF<sub>4</sub> leads to addition of the unsubstituted acetylene carbon to the internal olefin carbon. The result is rather unexpected because it was shown earlier that the addition of acetylenes to internal olefins was several times slower than addition of acetylenes to terminal olefins.<sup>2c</sup> The regioselectivity of this reaction indicated that the mechanisms of formation of **7** and **2–6** are different. A possible intermediate here could be the phenylvinylidene complex [Ru( $\eta^5:\eta^2-Me_4C_5CH_2OCH_2$ - Scheme 4

co CO Ru Ru P "E.E"-isomer "Z,E"-isomer Ηç Hb' R2 Hc' Нb Hc' Ha Hb" Ha' 11 3.6 阏 4.0 Q ÛÛ 44 4.8 ΰÛ 5.2 48 44 40 36 52

**Figure 4.** 2D EXSY <sup>1</sup>H NMR spectrum (region of the olefinic protons) of the mixture of isomers **2a**' and **2a**'' (400 MHz, acetone- $d_6$ , 300 K,  $\tau_m = 1$  s, initial delay 2 s, number of scans 256, a matrix 1024 × 256 was acquired by the TPPI technique and zero-filled to the size 1024 × 1024).

#### Scheme 5



CH=CH<sub>2</sub>)( $\eta^{1}$ -C=CHPh)(CO)]<sup>+</sup> by analogy with the reaction that was found recently.<sup>5</sup> The fact that protonation of [Ru( $\eta^{5}:\eta^{2}$ -Me<sub>4</sub>C<sub>5</sub>CH<sub>2</sub>OCH<sub>2</sub>CH=CH<sub>2</sub>)( $\eta^{1}$ -C=CPh)(CO)] (**8**) also gives **7** as a sole product is indirect support for this suggestion (Scheme 8).

## **Experimental Details**

**General Procedures.** All experiments were performed under argon in solvents purified by standard methods. <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained with Bruker AMX 400 and Varian VXR 400 spectrometers. All chemical shifts are reported in ppm ( $\delta$ ) with refer-



s-trans-isomer II

ence to TMS. IR spectra were obtained with Specord M-82. Microanalyses were performed by Laboratory of Microanalysis of the Institute of Organoelement Compounds. The chelate complex **1** was prepared according to literature methods.<sup>6</sup>

Interaction of 1 with Acetylenes in the Presence of AgBF<sub>4</sub> (General Procedure). Silver tetrafluoroborate (80 mg; 0.4 mmol) was added to a solution of 1 (140 mg; 0.4 mmol) and PhC=CH (100  $\mu$ L; 1 mmol) in CH<sub>2</sub>- $Cl_2$  (20 cm<sup>3</sup>) at -78 °C, stirred for 0.5 h, and then was allowed to warm to room temperature. The solution was filtered and concentrated to 2 cm<sup>3</sup>. Addition of ether precipitated a pale yellow solid, which was collected on a frit and dried in vacuo. Yield of 7: 210 mg (91%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 1.30 (s, 3H, Me); 1.74 (s, 3H, Me); 1.79 (s, 3H, Me); 2.06 (d, 1H, =CHH, J = 2.9 Hz); 2.31 (s, 3H, Me); 3.07 (d, 1H, =CH*H*, *J* = 2.9 Hz); 3.15 (d, 1H, OCHH, J = 14.7 Hz); 3.57 (d, 1H, Cp\*CHHO, J = 14.0Hz); 3.83 (d, 1H, =CHPh, J = 11.2 Hz); 4.51 (d, 1H, Cp\*CH*H*O, *J* = 14.0 Hz); 5.06 (d, 1H, OCH*H*, *J* = 14.7 Hz); 5.68 (d, =CH-, J = 11.2 Hz); 7.39 (s, 5H, C<sub>6</sub>H<sub>5</sub>).  $^{13}\text{C}$  NMR (CD\_2Cl\_2): 6.5 (Me); 7.9 (Me); 8.2 (Me); 9.4 (Me); 47.8 (CH<sub>2</sub>); 58.3 (CH<sub>2</sub>); 66.1 (CH<sub>2</sub>); 75.9 (CH); 82.5 (CH); 94.3 (C); 94.5 (C); 97.2 (C); 98.8 (C); 104.3 (C); 106.1 (C); 125.4 (CH); 127.4 (CH); 128.4 (CH); 131.7 (C); 204.0 (CO).

The diene complexes 2-6 were prepared by an analogous method. Their IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectra are given in Tables 1, 2 and 3, correspondingly.

Synthesis of  $[Ru(\eta^1-C=CPh)(\eta^2:\eta^5-Me_4C_5CH_2OC-H_2CH=CH_2)(CO)]$  (8). Solid PhC=CLi (32 mg, 0.30

Scheme 7







mmol) was added to solution of 1 (107 mg, 0.30 mmol) in THF (10 cm<sup>3</sup>) at 0 °C, and the mixture was stirred for 1 h. The solution was allowed to warm to room temperature, solvent was removed under vacuum, and the residue was crystallized from a mixture of petroleum ether and ether. Yield of 8: 87 mg, 69%. IR spectrum (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (C=C) 2098 and  $\nu$ (CO) 2069 cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): 1.44 (s, 3H, Me); 1.74 (s, 3H, Me); 1.88 (s, 3H, Me); 1.91 (s, 3H, Me); 2.04 (d, 1H, =CH*H*, *J* = 12.0 Hz); 2.84 (d, 1H, =C*H*H, *J* = 8.0 Hz); 3.05 (dd, 1H, OC*H*H, J = 15.0; J = 2.0 Hz); 3.33 (d, 1H, Cp\*CHHO, J = 13.0 Hz); 4.05 (d, 1H, Cp\*CH*H*O, *J* = 13.0 Hz); 4.06 (dddd, 1H, -CH =, J = 12.0, J = 8.0, J = 2.0, J = 1.0 Hz); 4.22 (dd, 1H, OC*H*H, J = 15.0; J = 1.0 Hz); 6.9–7.2 (m, 5H, Ph). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): 9.0 (Me); 10.0 (Me); 10.1 (Me); 10.4 (Me); 39.5 (=CH<sub>2</sub>); 62.1 (CH<sub>2</sub>); 66.1 (CH<sub>2</sub>); 68.0 (CH); 90.4 (C); 90.7 (C); 96.5 (C); 103.7 (C); 107.0 (C); 107.7 (C); 108.9 (C); 124.8 (CH); 128.2 (CH); 130.2 (CH); 131.6 (CH); 205.6 (CO).

**Protonation of** [Ru( $\eta^5:\eta^2$ -C<sub>5</sub>Me<sub>4</sub>CH<sub>2</sub>OCH<sub>2</sub>CH= CH<sub>2</sub>)( $\eta^1$ -C=CPh)(CO)] (8). A solution of Et<sub>2</sub>O·HBF<sub>4</sub> (50 mg, 0.3 mmol) in ether (5 cm<sup>3</sup>) was added dropwise to a solution of 8 (84 mg, 0.2 mmol) at -78 °C. The resultant solution was stirred for 0.5 h and then allowed to warm to room temperature. The solid precipitate was

Table 5. Crystal Data and Details of the X-rayExperiments for 2a" and 7

	2a″	7
formula	C <sub>28</sub> H <sub>29</sub> O <sub>2</sub> RuPF <sub>6</sub>	C22H25O2RuPF6
mol wt	643.55	567.46
cryst size, mm	$0.10 \times 0.20 \times 0.20$	0.15  imes 0.20  imes 0.25
cryst system	orthorhombic	orthorhombic
space group	$Pca2_1$	Pbca
cell constants	-	
a, Å	30.83(2)	16.847(4))
b, Å	8.103(5)	14.805(4)
c, Å	10.494(6)	18.318(5)
V, Å <sup>3</sup>	2622(3)	4569(2)
Z	4	8
$D_{\rm calc}$ , g cm <sup>-3</sup>	1.631	1.650
diffractometer	Siemens P3/PC	Siemens P3/PC
temp, K	153	153
radiation (Å)	Μο Κα	Μο Κα
	$(\lambda = 0.71073)$	$(\lambda = 0.71073)$
scan mode	$\theta - 2\theta$	$\theta - 2\theta$
$2\theta_{\rm max}$ , deg	56	55
tot unique reflns collcd	3220	5120
abs coeff, $\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	0.727	0.822
largest diff peak and hole, e·Å <sup>-3</sup>	0.692; -2.242	4.189; -0.822
R1 (on F for reflns	0.0445	0.0722
with $I > 2\sigma(I)$	(2420 reflns)	(3197 reflns)
wR2 (on $F^2$ for all reflns)	0.1233	0.1935
	(3147 reflns)	(4399 reflns)

filtered, washed with  $Et_2O$ , crystallized from  $CH_2Cl_2/$  $Et_2O$ , and dried in vacuo. Yield of **7**: 61 mg (60%).

**X-ray Data Collection, Structure Determination, and Refinement for 2a**" **and 7**. Single crystals of complexes [2a"]<sup>+</sup>PF<sub>6</sub><sup>-</sup> and [7]<sup>+</sup>PF<sub>6</sub><sup>-</sup> were grown at room temperature (25 °C) by a layering method, with dimethoxyethane added to the sample dissolved in methylene chloride. Accurate unit cell parameters and orientation matrixes were obtained by least-squares refinement of 24 carefully centered reflections in the 23°  $\leq \theta \leq 27^{\circ}$  range. Two standard reflections were monitored every 98 reflections for 2 and 7 and showed no significant variations in both cases. Data were corrected for Lorentz and polarization effects. Rather small, wellformed, and essentially isometric single crystals were carefully chosen. The quality of the results and the relatively low absorption coefficient values justified our not making absorption corrections.

The structures were solved by direct methods and subsequent difference Fourier maps. The difference Fourier synthesis for **7** revealed additional peaks which were interpreted as a disorder of the fluorine atoms of the  $PF_6^-$  anion. The occupancies of the positions of three fluorine sets (labeled F, F' and F'') were refined to 0.39, 0.35, and 0.26, respectively. The positions for all H atoms in both molecules were calculated geometrically and refined in the "ridding" approximation. All structures were refined by a full-matrix least-squares method against  $F^2$  in the anisotropic—isotropic (H atoms and fluorines of the disordered  $PF_6^-$  anion) approximation. The absolute structure in crystal of **2a**" was determined using the Flack parameter, which was equal to 0.08(14). All calculations were carried out on an IBM PC with SHELXTL PLUS 5 (gamma-version) programs. Crystal data and details of the X-ray experiments are given in Table 5.

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**Supporting Information Available:** Tables of atomic parameters, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for the crystal structures of  $[2a'']PF_6$  and  $[7]PF_6$  and figure of the 2D <sup>1</sup>H EXSY NMR spectrum (high-field region) for the mixture of isomers 2a' and 2a''. This material is available free of charge via the Internet at http://pubs.acs.org.

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