

were obtained from Aldrich and used as received. The a-PF and a-(Cl)<sub>2</sub>-CT-TPPFeCl porphyrins were synthesized as described in ref 32. CO<sub>2</sub> was of N45 grade from Alphasgas (Air Liquide).

**Cyclic Voltammetry and Thin-Layer UV-vis Spectroelectrochemistry.** The cells, instruments, and procedures used for cyclic voltammetry and thin-layer UV-vis spectroelectrochemistry were the same as previously described.<sup>33</sup> The UV-vis spectra were recorded on a Varian 2300 spectrophotometer. The working electrodes were a 3-mm diameter glassy carbon disk (frequently polished with diamond pastes down to 1 μm) or a mercury drop hung onto a gold disk in cyclic voltammetry and a 2.4 cm<sup>2</sup> platinum grid in spectroelectrochemistry. The reference electrode was a NaCl saturated calomel electrode. Dilution of CO<sub>2</sub> with argon was carried out by means of a mass flow regulator (Air liquide Alphasgas) allowing a constant partial pressure of CO<sub>2</sub> to be established.

**Preparative Scale Electrolysis Product Analysis.** We used a gas-tight cell allowing the CO<sub>2</sub> pressure to remain constant during the electrolysis similar to that described in ref 13l. The mercury pool cathode was vigorously agitated by means of a magnetic stirrer. A platinum wire separated from the cathodic compartment by a Nafion membrane or a magnesium wire were used as anodes. The reference electrode was again

a NaCl saturated calomel electrode. After saturation of the solution during 30 min by CO<sub>2</sub> dried over a CaCl<sub>2</sub> or silica gel column, the cell was isolated. The first electrolysis was carried out at the potential where the Fe(III) porphyrin is converted into its Fe(II) form. A second electrolysis was then performed at the potential where the Fe(II) porphyrins is converted into its Fe(I) form. These two preliminary electrolyses lasted about 10 min each. The potential was then set to the value where the catalysis takes place, i.e., the potential where the Fe(I) porphyrins are converted into the Fe("0") form. The electrolysis was pursued up to about 4 h. We assayed for CO and H<sub>2</sub> by means of gas chromatography on silica gel or Porapak columns. Formaldehyde was looked for by means of the chromotropic acid method.<sup>34a</sup> The same method was used for testing the possible presence of formate, after reduction of the acidified solution by magnesium.<sup>34b</sup> For testing the possible presence of oxalate we carried out a series of electrolyses in *n*-butyronitrile with *n*-Bu<sub>4</sub>NClO<sub>4</sub> as supporting electrolyte. By using *n*-butyronitrile, which is immiscible with water we could extract the oxalate ions from the organic phase and titrate them in the aqueous extract with a saturated solution of BaCl<sub>2</sub>. The production of CO in these electrolyses was essentially the same as in the electrolyses carried out in DMF.

**Acknowledgment.** We are indebted to Prof. Elio Vianello (Padova, Italy) for the communication of his results on the redox catalysis of the electrochemical reduction of CO<sub>2</sub><sup>2e</sup> prior to publication.

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## Ruthenium/Zirconium Complexes Containing C<sub>2</sub> Bridges with Bond Orders of 3, 2, and 1. Synthesis and Structures of Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH<sub>n</sub>CH<sub>n</sub>ZrClCp<sub>2</sub> (n = 0, 1, 2)

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**Abstract:** A series of Ru/Zr complexes linked by C<sub>2</sub> bridges of bond orders 3, 2, and 1 were prepared, and characterized by spectroscopic data and single-crystal X-ray diffraction. The dimetalloalkyne complex Cp(PMe<sub>3</sub>)<sub>2</sub>RuC≡CZrClCp<sub>2</sub> was prepared by the reaction of Cp(PMe<sub>3</sub>)<sub>2</sub>RuC≡CH with either Cp<sub>2</sub>Zr(CH<sub>3</sub>)Cl or Cp<sub>2</sub>Zr(NMe<sub>2</sub>)Cl. This dimetalloalkyne is the first example of a structurally characterized alkyne that is substituted by an electron-rich metal at one end, and by an electron-deficient metal at the other. The reaction of Cp(PMe<sub>3</sub>)<sub>2</sub>RuC≡CH with [Cp<sub>2</sub>Zr(H)Cl]<sub>n</sub> gives the dimetalloalkene complex Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CHZrClCp<sub>2</sub>, which has a three-center, two-electron agostic interaction between the Zr and the vinylic CH that is β to Zr. Carbonylation of Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CHZrClCp<sub>2</sub> with 1 atm of CO produces the η<sup>2</sup>-acyl complex Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CHC(O)ZrClCp<sub>2</sub>. Analysis of the spectroscopic and structural data for this acyl compound indicates a substantial contribution from a zwitterionic resonance form that has a formal positive charge at Ru and a negative charge on the Zr portion. Hydrolysis of Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CHZrClCp<sub>2</sub> produces the known zirconium complex [Cp<sub>2</sub>ZrCl]<sub>2</sub>O and the ruthenium vinyl complex Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CH<sub>2</sub>. Reaction of [Cp<sub>2</sub>Zr(H)Cl]<sub>n</sub> with Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CH<sub>2</sub> gives the dimetalloalkane complex Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH<sub>2</sub>CH<sub>2</sub>ZrClCp<sub>2</sub>. Spectroscopic and crystallographic data are interpreted to indicate that this compound also has an agostic interaction between the Zr and a CH adjacent to Ru.

Organometallic complexes in which two or more metals are linked by a hydrocarbon bridge have been studied extensively as models for species postulated to be present in several important metal-catalyzed reactions.<sup>1</sup> Detailed investigations of the ways in which metal-carbon and carbon-carbon bonds are made and broken in these soluble complexes can provide useful information for comparison to similar processes that occur in homogeneous catalytic reactions and on metal surfaces. Methylene-bridged

complexes are a thoroughly investigated class of C<sub>1</sub>-bridged complexes.<sup>2</sup> Most methylene-bridged complexes contain identical or similar metals bonded to the -CH<sub>2</sub>- bridge. Methylene-bridged complexes in which the -CH<sub>2</sub>- bridge links two metals of disparate electronic properties, though relatively rare, have proven to exhibit

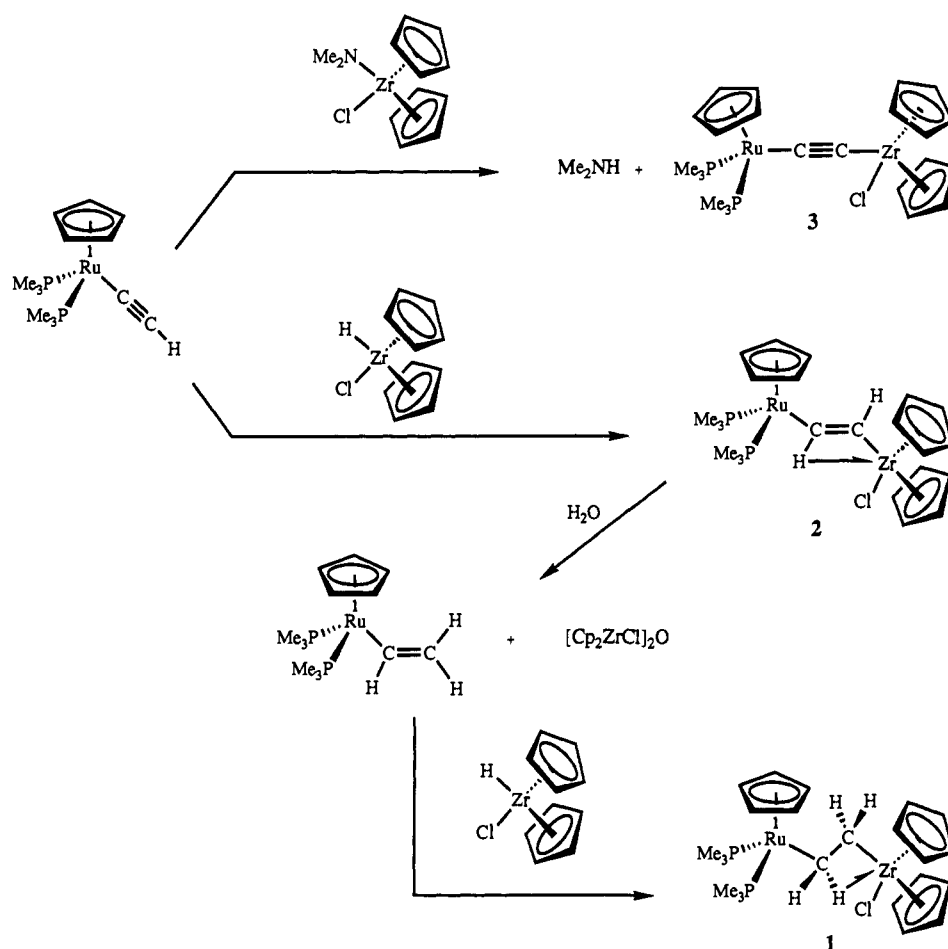
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Scheme I.



unusual reactions and structural features.<sup>3,4</sup>

Compared to the numerous methylene-bridged complexes, there are far fewer examples of compounds containing a -CH<sub>2</sub>CH<sub>2</sub>-bridge between two metals. Two-carbon bridges present the additional possibility of linking the two metals by C<sub>2</sub> bridges having different C-C bond orders. In this paper, we report the synthesis, spectra, and structures of a series of complexes in which an electron-rich metal fragment [Cp\*(PMe<sub>3</sub>)<sub>2</sub>Ru] is linked to an electron-deficient metal fragment [Cp<sub>2</sub>ZrCl] by C<sub>2</sub> bridges of bond orders 3, 2, and 1.<sup>5</sup> The availability of a complete series with RuC≡CZr, RuCH=CHZr, and RuCH<sub>2</sub>CH<sub>2</sub>Zr moieties provides a unique opportunity to compare the spectroscopic and structural properties of C<sub>2</sub>-bridged complexes with saturated and unsaturated two-carbon linkages. The preparation and complete characterization of an η<sup>2</sup>-acyl derivative of the RuCH=CHZr complex is also reported.

## Results

**Preparation of Ruthenium Alkynyl Complexes.** The ruthenium alkynyl complex Cp\*(PMe<sub>3</sub>)<sub>2</sub>Ru-C≡CH, which was utilized in the synthesis of the Ru/Zr dimetalloalkene and dimetalloalkyne complexes, was prepared by deprotonation of the cationic vinylidene complex [Cp\*(PMe<sub>3</sub>)<sub>2</sub>Ru=C=CH<sub>2</sub>]<sup>+</sup>[PF<sub>6</sub>]<sup>-</sup>. This re-

action was mentioned in an earlier communication<sup>6</sup> but was not described in detail; synthetic and spectroscopic data for the preparation of both Cp\*(PMe<sub>3</sub>)<sub>2</sub>Ru-C≡CH and Cp\*(PMe<sub>3</sub>)<sub>2</sub>Ru-C≡CCH<sub>3</sub> are provided in the Experimental Section.

**Preparation and Characterization of 1,2-Dimetalloalkynes.** The preparation of the C<sub>2</sub>-bridged Ru/Zr complexes of carbon-carbon bond orders 3, 2, and 1 is shown in Scheme I. (In this paper, 1, 2, and 3 will be used as abbreviations for the C<sub>2</sub>-bridged Ru/Zr compounds; the number refers to the bond order between the two carbons.) The dimetalloalkyne complex Cp\*(PMe<sub>3</sub>)<sub>2</sub>Ru-C≡CZrClCp<sub>2</sub> (3) was prepared by two related routes, both of which utilized Cp\*(PMe<sub>3</sub>)<sub>2</sub>Ru-C≡CH as the Ru starting material. The preparation shown in Scheme I involves reaction of Cp\*(PMe<sub>3</sub>)<sub>2</sub>Ru-C≡CH with Cp<sub>2</sub>Zr(NMe<sub>2</sub>)Cl, which was prepared in situ from Cp<sub>2</sub>ZrCl<sub>2</sub> and Cp<sub>2</sub>Zr(NMe<sub>2</sub>)<sub>2</sub>. In an NMR experiment, the reaction of Cp\*(PMe<sub>3</sub>)<sub>2</sub>Ru-C≡CH (~0.09 M) with Cp<sub>2</sub>ZrCl<sub>2</sub> (~0.04 M) and Cp<sub>2</sub>Zr(NMe<sub>2</sub>)<sub>2</sub> (~0.04 M) occurred slowly at 55 °C in C<sub>6</sub>D<sub>6</sub>, taking over 1 week to reach completion. In preparative reactions, this synthesis was carried out at 100 °C in toluene.

The two mononuclear zirconium species, Cp<sub>2</sub>ZrCl<sub>2</sub> and Cp<sub>2</sub>Zr(NMe<sub>2</sub>)<sub>2</sub>, undergo a ligand redistribution reaction to give Cp<sub>2</sub>Zr(NMe<sub>2</sub>)Cl. This reaction was examined separately (in the absence of any Cp\*(PMe<sub>3</sub>)<sub>2</sub>Ru-C≡CH) at room temperature; the equilibrium requires several days to be established. The equilibrium constant was not measured, but qualitatively it is clear that it significantly favors the Cp<sub>2</sub>Zr(NMe<sub>2</sub>)Cl species, as found by Jordan<sup>7</sup> for several related redistribution reactions of Cp<sub>2</sub>ZrCl<sub>2</sub> with Cp<sub>2</sub>Zr(CH<sub>3</sub>)<sub>2</sub>, etc. The successful implementation of this synthesis requires that the reaction of Cp\*(PMe<sub>3</sub>)<sub>2</sub>Ru-C≡CH with Cp<sub>2</sub>Zr(NMe<sub>2</sub>)Cl be much faster than that of Cp\*(PMe<sub>3</sub>)<sub>2</sub>Ru-C≡

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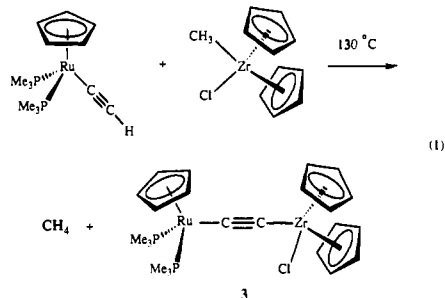
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**Table I.** Crystallographic Data from the X-ray Diffraction Study of 1, 2, 3, and 2-CO

	compound			
	1	2	3	2-CO
formula	C <sub>23</sub> H <sub>37</sub> ClP <sub>2</sub> RuZr	C <sub>23</sub> H <sub>35</sub> ClP <sub>2</sub> RuZr	C <sub>23</sub> H <sub>33</sub> ClP <sub>2</sub> RuZr	C <sub>24</sub> H <sub>35</sub> ClOP <sub>2</sub> RuZr
<i>a</i> , Å	11.906 (3)	8.173 (6)	8.748 (1)	16.387 (4)
<i>b</i> , Å	14.001 (5)	14.679 (5)	12.839 (8)	14.364 (4)
<i>c</i> , Å	15.203 (5)	20.727 (5)	11.653 (5)	11.248 (8)
β, deg	99.83 (2)		110.21 (3)	
<i>V</i> , Å <sup>3</sup>	2497 (2)	2486 (3)	1228 (2)	2647 (3)
<i>Z</i>	4	4	2	4
mol wt	603.24	601.16	599.20	629.17
space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>Pnma</i>	<i>P</i> 2 <sub>1</sub> / <i>m</i>	<i>Pnma</i>
ρ(calcd), g cm <sup>-3</sup>	1.604	1.606	1.620	1.578
radiation	Mo Kα (graphite monochromatized)	Mo Kα (graphite monochromatized)	Mo Kα (graphite monochromatized)	Mo Kα (graphite monochromatized)
μ, cm <sup>-1</sup>	12.4	12.4	12.6	11.8
transmission coeff (max, min)	0.8340, 0.7299	0.7968, 0.7746	0.8857, 0.6200	0.8224, 0.7507
<i>R</i>	0.055	0.075	0.068	0.065
<i>R<sub>w</sub></i>	0.067	0.098	0.086	0.088
max shift/error, final cycle	≤0.01	≤0.01	≤0.01	≤0.003
temperature, K	200	200	200	200

CH with Cp<sub>2</sub>Zr(NMe<sub>2</sub>)<sub>2</sub>. Accordingly, little reaction was observed when a C<sub>6</sub>D<sub>6</sub> solution of Cp(PMe<sub>3</sub>)<sub>2</sub>RuC≡CH (~0.09 M) and Cp<sub>2</sub>Zr(NMe<sub>2</sub>)<sub>2</sub> (~0.04 M) was heated at 80 °C for 6 days.

Another synthetic route to 3 utilizes Cp<sub>2</sub>Zr(CH<sub>3</sub>)Cl as the Zr starting material. When a toluene solution of Cp(PMe<sub>3</sub>)<sub>2</sub>RuC≡CH and Cp<sub>2</sub>Zr(CH<sub>3</sub>)Cl was heated for several days in a sealed tube at 130 °C, methane and the dimetalloalkyne complex 3 were produced (eq 1).



The high-temperature conditions utilized in the synthesis of 3 attest to its thermal stability. In fact, less than 25% decomposition was observed by <sup>1</sup>H NMR when a 0.05 M solution of 3 in toluene-*d*<sub>8</sub> was heated at 130 °C for 3 weeks. In contrast to this thermal stability, however, solutions of 3 are extremely sensitive to trace amounts of water, resulting in hydrolysis to regenerate the ruthenium alkynyl complex Cp(PMe<sub>3</sub>)<sub>2</sub>RuC≡CH. Although all of the Ru/Zr complexes reported in this paper exhibit an expected sensitivity to air and water, qualitative observations indicate that the dimetalloalkyne complex 3 is more sensitive to hydrolysis by traces of water than either 2 or 1.

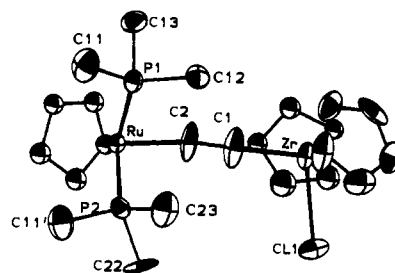
The two carbons of the C<sub>2</sub> bridge of 3 appear in the <sup>13</sup>C NMR at similar positions. The ZrC resonance appears as a singlet at δ 190.4, and the RuC resonance is a triplet (<sup>2</sup>*J*<sub>PC</sub> = 22.8 Hz) at δ 178.3. A strong band in the IR spectrum at 1868 cm<sup>-1</sup> is assigned to the C≡C stretch.

The structure of the dimetalloalkyne complex was determined by single-crystal X-ray diffraction. Details of the data collection and refinement parameters are provided in Table I. Table II lists some of the pertinent bond distances and angles for this compound, along with comparisons to the related RuCH=CHZr and RuC-H<sub>2</sub>CH<sub>2</sub>Zr complexes. The Ru atom is disordered about the mirror plane; details of the disorder are given in the Experimental Section. An ORTEP drawing of one molecule of the disordered pair is shown in Figure 1.

The ruthenium alkynyl complex Cp(PMe<sub>3</sub>)<sub>2</sub>RuC≡CH was also used in the preparation of an alkyne substituted at one end by a transition metal (Ru) and at the other end by a main group element (Sn). The reaction of Cp(PMe<sub>3</sub>)<sub>2</sub>RuC≡CH with excess Me<sub>3</sub>SnNMe<sub>2</sub> at room temperature produced Cp(PMe<sub>3</sub>)<sub>2</sub>RuC≡

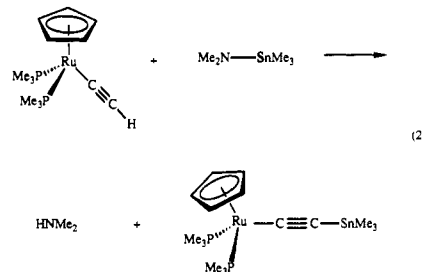
**Table II.** Comparison of Structural Data for Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH<sub>2</sub>-CH<sub>2</sub>Zr(Cl)Cp<sub>2</sub>, Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CHZr(Cl)Cp<sub>2</sub>, and Cp(PMe<sub>3</sub>)<sub>2</sub>RuC≡CZr(Cl)Cp<sub>2</sub> Complexes

	RuCH <sub>2</sub> CH <sub>2</sub> Zr			RuCH=CHZr			RuC≡CZr		
	1	2	3	1	2	3	1	2	3
Ru-C(2), Å	2.186 (9)	2.095 (16)	1.989 (13)						
Zr-C(1), Å	2.276 (10)	2.185 (19)	2.141 (15)						
C-C, Å	1.485 (14)	1.304 (22)	1.251 (20)						
Zr...C(2)	2.549 (9)	2.564 (17)							
Ru-C-C angle, deg	118.2 (7)	144 (1)	169.9 (3)						
Zr-C-C angle, deg	82.5 (6)	91 (1)	174 (2)						
C(1)-Zr-Cl	117.4 (3)	116.2 (5)	103.3 (2)						
P-Ru-P angle, deg	95.7 (1)	98.7 (2)	95.9 (2)						

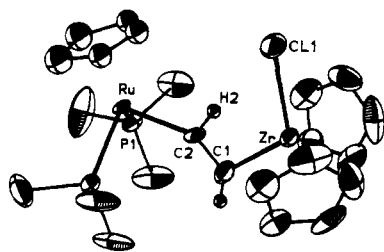


**Figure 1.** ORTEP drawing of Cp(PMe<sub>3</sub>)<sub>2</sub>RuC≡CZr(Cl)Cp<sub>2</sub> (3) showing 50% probability thermal ellipsoids. The molecule is disordered about the mirror plane containing C(2), C(1), and Zr; the Ru atom lies about 0.3 Å from this plane. The elongated thermal ellipsoids of C(2), C(1), and Zr indicate that these atoms are also slightly disordered about the mirror plane.

CSnMe<sub>3</sub>. The IR band at 1919 cm<sup>-1</sup> assigned to the C≡C stretch appears at a higher stretching frequency than that of dimetalloalkyne 3, and the <sup>13</sup>C NMR peaks for the alkyne carbons (δ 145.3 for RuC; δ 102.3 for SnC) are considerably upfield from those found for dimetalloalkyne 3.



**Preparation and Characterization of Dimetalloalkenes.** The reaction (Scheme I) of Cp(PMe<sub>3</sub>)<sub>2</sub>RuC≡CH with [Cp<sub>2</sub>Zr(H)Cl]<sub>n</sub> gives Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CHZrClCp<sub>2</sub> (2). The <sup>3</sup>*J*<sub>HH</sub> = 18.8 Hz



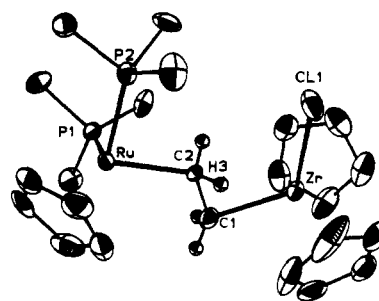
**Figure 2.** ORTEP drawing of  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{CHZrClCp}_2$  (**2**) showing 50% probability thermal ellipsoids. The atoms Ru, C(2), C(1), Zr, and Cl lie on a crystallographic mirror plane.

coupling between the two vinyl protons of **2** indicates the trans geometry of the dimetalloalkene. Differences in the P–H coupling constants facilitate the assignment of the resonance at  $\delta$  9.46 ( $^3J_{\text{PH}} = 4.3$  Hz) as that for the  $\text{RuCH}$ , while the resonance at  $\delta$  8.38 ( $^4J_{\text{PH}} = 0.8$  Hz) is due to the  $\text{ZrCH}$ . In the  $^{13}\text{C}$  NMR spectrum, the  $\text{ZrC}$  resonance at  $\delta$  198.7 ( $^3J_{\text{PC}} = 4$  Hz) exhibits a C–H coupling constant of  $^1J_{\text{CH}} = 157$  Hz. The much smaller  $^1J_{\text{CH}}$  of 110 Hz observed for the  $\text{RuCH}$  resonance at  $\delta$  114.7 ( $^2J_{\text{PC}} = 16$  Hz) suggests a three-center, two-electron agostic<sup>8</sup> bonding interaction between this CH and the Zr center. Additional evidence in support of this agostic interaction comes from a low-intensity, broad IR band centered around 2590  $\text{cm}^{-1}$  in the IR spectrum of **2**, which is assigned to the agostic C–H stretch. This assignment is confirmed by the absence of this band in the deuterium-labeled derivative  $\text{Cp}(\text{PMe}_3)_2\text{RuCD}=\text{CHZrClCp}_2$  (prepared from the reaction of  $\text{Cp}(\text{PMe}_3)_2\text{RuC}\equiv\text{CH}$  with  $[\text{Cp}_2\text{Zr}(\text{D})\text{Cl}]_n$ ) in which it is replaced by a sharper band at 1900  $\text{cm}^{-1}$  assigned to the C–D stretch.

The reaction of the propynyl complex  $\text{Cp}(\text{PMe}_3)_2\text{RuC}\equiv\text{CCH}_3$  with  $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]_n$  provided the corresponding methyl-substituted dimetalloalkene complex  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{CMeZrClCp}_2$ . Spectroscopic data for this complex were similar to those for **2**. In particular, the  $^1J_{\text{CH}}$  of 116 Hz observed for the  $\text{RuCH}$  resonance and the IR band at 2624  $\text{cm}^{-1}$  (shifted to 1914  $\text{cm}^{-1}$  in the deuterated derivative  $\text{Cp}(\text{PMe}_3)_2\text{RuCD}=\text{CMeZrClCp}_2$ ) again indicated an agostic interaction.

Details of the data collection and refinement parameters for the crystallographic study of **2** are given in Table I. Some of the pertinent bond distances and angles for this structure are given in Table II, and an ORTEP view is shown in Figure 2. There is a crystallographically imposed mirror plane that requires Ru, C(2), C(1), Zr, and Cl to reside in the same plane. The hydrogens on the carbons bonded to Ru and Zr were located on the difference Fourier map and are also in the mirror plane. The distance from H(2) to Zr is 2.08 (2) Å, but the accuracy of this distance suffers from the normal uncertainties involved in hydrogen atom locations determined by X-ray diffraction.<sup>9</sup> Along with the structural and spectroscopic data mentioned above, the presence of the agostic interaction between H(2) and Zr is further substantiated by the small Zr–C(1)–C(2) angle of 91 (1)°, which is far smaller than the 144 (1)° found for the Ru–C(2)–C(1) angle. The C(1)–Zr–Cl angle in **2** is nearly identical with that found in **1** (see below) but is about 13° larger than that found for **3**. Since an agostic interaction takes up a coordination site at the central position of the bent sandwich zirconocene structures in **2** and **1**, the C(1)–Zr–Cl angle is larger in these compounds compared to that in **3**, which has no ligand at the central position.

**Preparation and Characterization of a Ruthenium Vinyl Complex.** Addition of water to a THF solution of **2** produces the ruthenium vinyl complex  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{CH}_2$  and the oxygen-bridged zirconium dimer  $[\text{Cp}_2\text{ZrCl}]_2\text{O}$ ,<sup>10</sup> which precipitates from solution (Scheme I). The stoichiometry of this reaction requires only 0.5 equiv of water, so rigorous drying of solvents



**Figure 3.** ORTEP drawing of  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}_2\text{CH}_2\text{ZrClCp}_2$  (**1**) showing 50% probability thermal ellipsoids. The atoms Ru, C(2), C(1), Zr, and Cl lie within  $\pm 0.05$  Å of a noncrystallographic mirror plane.

and glassware is required in order to avoid unintentional hydrolysis of this (and other) complexes containing Zr–C bonds. The ruthenium vinyl complex can be isolated as a waxy yellow solid by hexane extraction followed by sublimation. This reaction can be carried out on isolated samples of **2**, but we normally prepared it by hydrolysis of solutions of **2** prepared according to Scheme I, without isolation of **2**. Isolated yields of  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{CH}_2$  (based on two steps from  $\text{Cp}(\text{PMe}_3)_2\text{RuC}\equiv\text{CH}$ ) ranged from 52% to 70%. The  $^1\text{H}$  NMR resonance for each of the three vinyl protons of  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{CH}_2$  appears as a doublet of doublet of triplets, since each vinyl proton is coupled to the other two vinyl protons as well as to the two phosphines. The monodeuterated complex  $\text{Cp}(\text{PMe}_3)_2\text{RuCD}=\text{CH}_2$  was isolated from hydrolysis of  $\text{Cp}(\text{PMe}_3)_2\text{RuCD}=\text{CHZrClCp}_2$ .

This ruthenium vinyl complex,  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{CH}_2$ , can also be prepared in high yield from alcoholysis of **2** by methanol or ethanol. This method is not useful for preparative reactions, however, since we were unable to separate  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{CH}_2$  from the zirconium products  $\text{Cp}_2\text{ZrCl}(\text{OCH}_3)$  or  $\text{Cp}_2\text{ZrCl}(\text{OCH}_2\text{CH}_3)$ .

**Preparation and Characterization of a 1,2-Dimetalloalkene.** In a reaction similar to formation of the dimetalloalkene, the reaction of  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{CH}_2$  with  $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]_n$  gives a dimetalloalkane complex,  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}_2\text{CH}_2\text{ZrClCp}_2$  (**1**), as an orange solid (Scheme I). Both of the  $\text{CH}_2$  resonances appear as unresolved multiplets in the  $^1\text{H}$  NMR spectrum, but definitive assignment of the resonance at  $\delta$  1.39 as  $\text{ZrCH}_2$  and that at  $\delta$  –0.05 as  $\text{RuCH}_2$  comes from a comparison of the spectrum of **1** with deuterated analogues. The monodeuterated dimetalloalkane complex  $\text{Cp}(\text{PMe}_3)_2\text{RuCHDCH}_2\text{ZrClCp}_2$  was prepared by two different routes: from reaction of  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{CH}_2$  with  $[\text{Cp}_2\text{Zr}(\text{D})\text{Cl}]_n$ , and from reaction of  $\text{Cp}(\text{PMe}_3)_2\text{RuCD}=\text{CH}_2$  with  $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]_n$ . The dideuterated complex  $\text{Cp}(\text{PMe}_3)_2\text{RuCD}_2\text{CH}_2\text{ZrClCp}_2$  was prepared from reaction of  $\text{Cp}(\text{PMe}_3)_2\text{RuCD}=\text{CH}_2$  with  $[\text{Cp}_2\text{Zr}(\text{D})\text{Cl}]_n$ . The two  $\text{CH}_2$  carbons of **1** appear at very different positions in the  $^{13}\text{C}$  NMR spectrum:  $\delta$  53.9 ( $^1J_{\text{CH}} = 145$  Hz) for  $\text{ZrCH}_2$  and  $\delta$  –34.4 ( $^1J_{\text{CH}} = 111$  Hz) for  $\text{RuCH}_2$ . As in the case of the related dimetalloalkene complex, we interpret the low  $^1J_{\text{CH}}$  for  $\text{RuCH}$  in this dimetalloalkane complex as being indicative of an agostic interaction between one of the CH's adjacent to Ru with the unsaturated Zr center. Supporting spectroscopic evidence for this comes from an IR band at 2743  $\text{cm}^{-1}$  in the  $\text{RuCH}_2\text{CH}_2\text{Zr}$  complex, which is appropriately shifted to 2031  $\text{cm}^{-1}$  in the  $\text{RuCD}_2\text{CH}_2\text{Zr}$  analogue.

The structure of the dimetalloalkane complex **1** was determined by X-ray crystallography. Details of the data collection and refinement parameters are provided in Table I. Table II lists some of the important bond distances and angles for this structure, and an ORTEP drawing is shown in Figure 3. The M–C(sp<sup>3</sup>) distances of **1** are longer than the M–C(sp<sup>2</sup>) distances of **2**: Both the Zr–C and the Ru–C distances are about 0.09 Å longer in **1** compared to those in **2**. There is no crystallographically imposed mirror plane in **1**, but Ru, C(2), C(1), Zr, and Cl are nearly coplanar. The largest deviation from the best plane containing these five atoms is –0.05 Å for C(2). The agostic hydrogen, H(3), lies 0.70 Å out of this plane. The distance from Zr to H(3) is 2.19 (2) Å.

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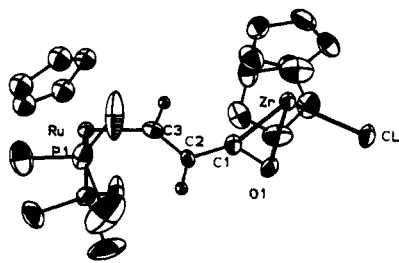
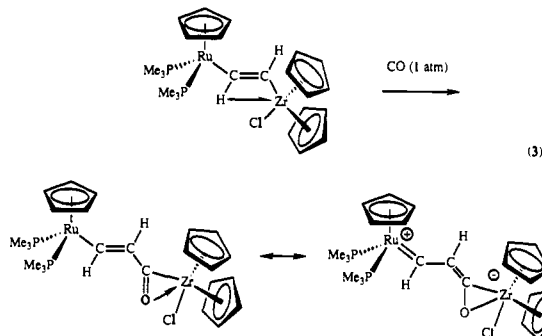


Figure 4. ORTEP drawing of  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{CHC}(\text{O})\text{ZrClCp}_2$  (**2-CO**) showing 50% probability thermal ellipsoids. The atoms Ru, C(3), C(2), C(1), O(1), Zr, and Cl lie on a crystallographic mirror plane.

Insertion of CO into the Zr–C Bonds of  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{CRZrClCp}_2$  ( $\text{R} = \text{H}, \text{CH}_3$ ). When a THF solution of **2** was stirred under CO (1 atm) overnight, an insertion of CO into the Zr–C bond occurred, and  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{CHC}(\text{O})\text{ZrClCp}_2$  (**2-CO**) was isolated in good yield (eq 3). The acyl is  $\eta^2$ -bonded to Zr,



as is generally the case for electron-deficient early transition metal acyl complexes.<sup>11</sup> Spectroscopic data indicative of the  $\eta^2$ -acyl include a singlet at  $\delta$  267.5 in the  $^{13}\text{C}$  NMR spectrum assigned to the acyl carbon, and an IR band at  $1443\text{ cm}^{-1}$  assigned to the C=O stretch. The NMR data are also consistent with a considerable contribution from the zwitterionic resonance form shown in eq 3, which has a cationic ruthenium carbene and a negative charge on zirconium. Specific evidence for the viability of the ruthenium carbene character in this complex comes from the observation of downfield shifts of the RuCH at  $\delta$  11.70 ( $^1J_{\text{HH}} = 15.8\text{ Hz}$ ,  $^3J_{\text{PH}} = 8.6\text{ Hz}$ ) in the  $^1\text{H}$  NMR spectrum as well as the  $^{13}\text{C}$  NMR resonance at  $\delta$  246.5 ( $^1J_{\text{CH}} = 131\text{ Hz}$ ) assigned to the RuCH.

The structure of the acyl complex **2-CO** was determined by X-ray crystallography. Data collection and refinement parameters are given in Table I, and bond distances and angles are listed in Table III. An ORTEP diagram is shown in Figure 4. There is a crystallographically imposed mirror plane that constrains Ru, C(3), C(2), C(1), O(1), Zr, and Cl to reside in the same plane. The  $\eta^2$ -bonding of the acyl to Zr deduced from solution spectroscopic data is verified to be maintained in the solid state. Along with the spectroscopic data mentioned above, the details of the structural determination also support a substantial contribution from both of the resonance forms shown in eq 3, as discussed in a later section.

Carbonylation of the methyl-substituted complex  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{C}(\text{CH}_3)\text{ZrClCp}_2$  produced an analogous  $\eta^2$ -acyl derivative,  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{ZrClCp}_2$ . Qualitative observations in separate reactions indicated that the rate of the carbonylation of **2** was much faster than the rate of carbonylation of the methyl derivative  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{C}(\text{CH}_3)\text{ZrClCp}_2$ . A competition experiment was carried out in which a  $\text{CD}_2\text{Cl}_2$  solution containing **2** and  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{C}(\text{CH}_3)\text{ZrClCp}_2$  was treated with CO. This experiment indicated a kinetic preference of  $\sim 100:1$  for reaction of CO with **2** compared to the closely related methyl derivative  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{C}(\text{CH}_3)\text{ZrClCp}_2$ . A similar kinetic preference is found for the reaction of  $^i\text{BuNC}$  with these

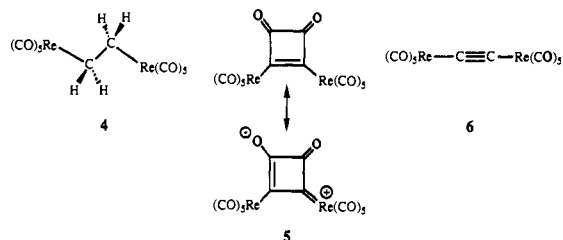
Table III. Selected Bond Lengths (Å) and Angles (deg) for  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{CHC}(\text{O})\text{ZrClCp}_2$  (**2-CO**)

Bond Lengths			
Ru–P(1)	2.256 (3)	Zr–C(1)	2.178 (12)
Ru–C(3)	1.977 (13)	Zr–Cl	2.577 (4)
C(3)–C(2)	1.352 (17)	Zr–O(1)	2.212 (9)
C(2)–C(1)	1.413 (16)	C(1)–O(1)	1.278 (15)
C(1)–O(1)	1.278 (15)		
Bond Angles			
P(1)–Ru–P(1')	98.2 (2)	Cl–Zr–C(1)	114.1 (4)
P(1)–Ru–C(3)	90.7 (2)	Cl–Zr–O(1)	80.3 (3)
Ru–C(3)–C(2)	137.9 (9)	C(1)–O(1)–Zr	71.6 (7)
C(3)–C(2)–C(1)	119 (1)	C(1)–Zr–O(1)	33.8 (4)
C(2)–C(1)–O(1)	127 (1)		

two dimetalloalkene complexes.<sup>12</sup> The fact that the spectroscopic data for the two acyl complexes are very similar is not surprising, but this similarity contrasts with the substantial differences in spectroscopic and structural properties of  $\eta^2$ -iminoacyl complexes that result from reaction of  $^i\text{BuNC}$  with  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{CRZrClCp}_2$  ( $\text{R} = \text{H}$  vs  $\text{R} = \text{CH}_3$ ).<sup>12</sup>

## Discussion

The  $\text{RuC}\equiv\text{CZr}$ ,  $\text{RuCH}=\text{CHZr}$ , and  $\text{RuCH}_2\text{CH}_2\text{Zr}$  complexes reported herein provide a unique set of complexes in which two carbons connect an electron-deficient metal with an electron-rich metal. Most of the previously reported complexes with two-carbon bridges have identical metals on the two sides of the linking  $\text{C}_2$  unit. The availability of spectroscopic and structural data for all three members of our series enables comparisons of these compounds with each other, as well as with other  $\text{C}_2$ -bridged complexes reported in the literature. In the following sections, the structural and spectroscopic properties of **3**, **2**, and **1** will be compared with related compounds of each type containing  $\text{MC}\equiv\text{CM}$ ,  $\text{MCH}=\text{CHM}$ , and  $\text{MCH}_2\text{CH}_2\text{M}$  moieties. We first briefly consider some general trends in the structures of our complete series of Ru/Zr complexes in comparison to a series of compounds reported by Beck and co-workers in which two Re( $\text{CO}$ )<sub>5</sub> moieties are linked by  $\text{C}_2$  bridges of bond orders 1,<sup>13</sup> 2,<sup>14</sup> and 3.<sup>15</sup> Table II shows a trend of decreasing Ru–C and Zr–C bond distances with increasing carbon–carbon bond order for our Ru/Zr compounds. An analogous trend was found in Beck's Re complexes where the Re–C distances in **4**, **5**, and **6** were 2.304



(**8**), 2.18 (1), and 2.141 (16) Å, respectively. Comparison of the bond lengths of the dimetallocyclobutenedione **5** with other members of the series is compromised by the influence of zwitterionic resonance forms, such as the one shown above with a  $\text{Re}=\text{C}$  double bond and a  $\text{C}-\text{C}$  single bond. To our knowledge, there are no other sets of  $\text{C}_2$ -bridged bimetallic complexes where all three members of the series are available for comparison.

**Comparison of  $\text{Cp}(\text{PMe}_3)_2\text{RuC}\equiv\text{CZrClCp}_2$  with Other  $\text{C}_2$ -Bridged Complexes.** Three ways in which a  $\text{C}_2$  unit can link two<sup>16</sup>

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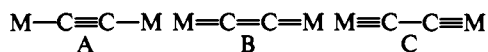
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Table IV. Spectroscopic and Structural Data for C<sub>2</sub>-Bridged Transition Metal Complexes

C <sub>2</sub> -bridged complex	$\nu(\text{C}\equiv\text{C}), \text{cm}^{-1}$	<sup>13</sup> C NMR of C≡C, ppm	C-C distance, Å	ref
(CO) <sub>3</sub> ReC≡CRu(CO) <sub>3</sub>	2002	94.4	1.19 (3)	15
Cp(CO) <sub>2</sub> RuC≡CRu(CO) <sub>2</sub> Cp		74.7	1.19 (1)	19
(PMe <sub>3</sub> ) <sub>2</sub> (I)PtC≡CPT(I)(PMe <sub>3</sub> ) <sub>2</sub>	2022		1.179 (48)	20
Cp*(CO) <sub>2</sub> FeC≡CFe(CO) <sub>2</sub> Cp*		98.1		21
(PPh <sub>3</sub> )AuC≡CAu(PPh <sub>3</sub> )	2040			22
Cp(CO) <sub>3</sub> WC≡CW(CO) <sub>3</sub> Cp			1.18 (3)	23
Cp* <sub>2</sub> ScC≡CScCp* <sub>2</sub>	1899	179.4	1.224 (9)	24
( <sup>1</sup> Bu <sub>3</sub> SiO) <sub>3</sub> Ta=C=C-Ta(OSi <sup>1</sup> Bu <sub>3</sub> ) <sub>3</sub>	1617		1.37 (4)	25
Cp(PMe <sub>3</sub> ) <sub>2</sub> RuC≡CZrClCp <sub>2</sub>	1868	178.3 (RuC) 190.4 (ZrC)	1.251 (20)	this work

transition metals are shown in generalized form below. A comparison of types A and B is given below. Type C will not be discussed in detail; an example of this type of C<sub>2</sub> bridge is (Me<sub>3</sub>CO)<sub>3</sub>W=CC=W(OCMe<sub>3</sub>)<sub>3</sub>.<sup>17</sup>



Frank and Selegue<sup>18</sup> recently reported a series of RuC≡CW and FeC≡CW complexes. One of their compounds, Cp-(PMe<sub>3</sub>)<sub>2</sub>RuC≡CW(CO)( $\eta^2$ -PhC≡CPh), has the same ligands on Ru as 3, but structural data are not available for comparison. Table IV lists spectroscopic and structural data associated with the C≡C moiety of several previously reported dimetalloalkyne complexes, along with comparative data for Cp(PMe<sub>3</sub>)<sub>2</sub>RuC≡CZrClCp<sub>2</sub> and (<sup>1</sup>Bu<sub>3</sub>SiO)<sub>3</sub>Ta=C=C-Ta(OSi<sup>1</sup>Bu<sub>3</sub>)<sub>3</sub>.<sup>25</sup> The average C=C distance<sup>26</sup> found in organic alkynes is 1.18 Å. This is similar to the C=C distances found for the ReC≡CRu, RuC≡CRu, PtC≡CPT, and WC≡CW complexes in Table IV. Both the <sup>13</sup>C NMR data as well as the  $\nu_{\text{C}\equiv\text{C}}$  stretching frequencies (from Raman data for the symmetrically substituted ReC≡CRu, PtC≡CPT, and AuC≡CAu compounds) are similar to spectroscopic data found in organic alkynes. These spectroscopic and structural data distinguish these dimetalloalkynes with resonance form M-C≡C-M from the alternative "dicarbide" M=C=C=M structure found in the Ta=C=C-Ta complex reported by Wolczanski and co-workers.<sup>25</sup> The  $\nu_{\text{C}\equiv\text{C}}$  stretching frequency of dimetalloalkyne 3 appears at 1868 cm<sup>-1</sup>, a value intermediate between those found for the C≡C stretch of the M-C≡C-M complexes and that found for the C=C stretch of the Ta=C=C-Ta complex. The <sup>13</sup>C NMR resonances of dimetalloalkyne 3 are considerably downfield of analogous resonances in the M-C≡C-M complexes, consistent with some metal carbene character of both in the bridging carbons in dimetalloalkyne 3. Although zirconocene complexes with Zr=C bonds are rare, Schwartz and Gell have reported<sup>27</sup> the spectroscopic characterization of thermally unstable Cp<sub>2</sub>(PMePh<sub>2</sub>)Zr=CH<sub>2</sub>. The <sup>13</sup>C NMR resonance at  $\delta$  248.6 for the carbene carbon of this mononuclear compound can be compared with the ZrC of dimetalloalkyne 3, which was observed at  $\delta$  190.4.

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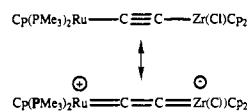
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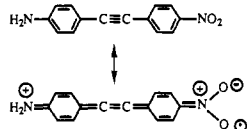
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Although the Ru-C distance (1.989 (13) Å) is not significantly shorter than the 2.016 (3) Å length found in ruthenium alkynyl complex Cp(PPh<sub>3</sub>)<sub>2</sub>RuC≡CPh,<sup>28</sup> the Zr-C distance (2.141 (15) Å) is considerably shorter than the Zr-C distance of 2.249 (3) Å determined<sup>29</sup> for Cp<sub>2</sub>Zr(C≡CMe)<sub>2</sub>. On the basis of the spectroscopic and structural data, we suggest that the zwitterionic resonance form shown below is a contributor to the structure of dimetalloalkyne 3. The intramolecular charge transfer required



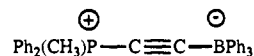
to convert this complex from the M-C≡C-M resonance form to the zwitterionic M=C=C=M resonance form is facilitated by the disparity in electronic structures of the electron-rich Ru fragment and the electron-deficient Zr fragment.

Compounds in which electron donors are linked to electron acceptors by an unsaturated bridge are of interest due to their potential utility in nonlinear optical applications. A caveat to the interpretation of the spectroscopic and structural results given above for these organometallic complexes is provided by a study<sup>30</sup> of organic alkynes substituted by donor and acceptor aromatic groups, such as (*p*-amino-*p*'-nitrodiphenyl)acetylene shown below.



Structural distortions indicative of the intramolecular charge transfer in this molecule were manifested primarily in the nitrophenyl and aminophenyl groups, and not in the acetylene linkage itself. The C≡C distance in this molecule was 1.183 (4) Å, thus showing no elongation of the carbon-carbon distance indicative of the distortion to the zwitterionic quinoid resonance structure.

Both the transition-metal organometallic "push-pull" acetylene 3 as well as the organic acetylene discussed above have C≡C units substituted by an electron donor at one end and an electron acceptor at the other end. Their zwitterionic resonance forms have the C=C cumulene type of structure. In contrast, Bestmann and co-workers have reported<sup>31</sup> the synthesis and structure of the phosphinoboratoacetylene shown below, which has a zwitterionic structure in the P-C≡C-B form. The C≡C bond distance of this compound is 1.216 (5) Å, consistent with the assignment as a triple bond.



**Formation and Stereochemistry of Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CZrClCp<sub>2</sub>.** Davison and Selegue have shown<sup>32</sup> that metal

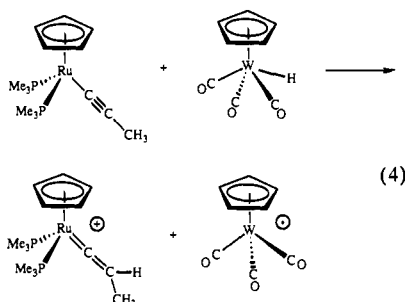
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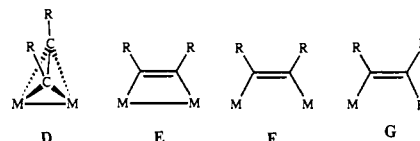
alkynyls and other unsaturated carbon ligands bonded to late transition metals generally undergo attack at the  $\beta$ -carbon by electrophiles, and attack at the  $\alpha$ -carbon by nucleophiles. Since some metal carbonyl hydrides are moderately acidic<sup>33</sup> whereas most early metal hydrides are hydridic,<sup>34</sup> we were interested in reacting the same metal alkynyl complex with both types of metal hydrides. On the basis of the established trends in reactivity of metal alkynyl complexes and metal hydrides, it was anticipated that the two different types of metal hydrides would lead to different types of products, with acidic metal hydrides protonating the  $\beta$ -carbon of the metal alkynyl complex, and hydridic metal hydrides delivering their H to the  $\alpha$ -carbon of the metal alkynyl complex. Prior to the study of the reaction of ruthenium alkynyl complexes with zirconium hydrides reported herein, we examined the reaction of  $\text{Cp}(\text{PMe}_3)_2\text{RuC}\equiv\text{CCH}_3$  with metal carbonyl hydrides.<sup>35</sup> Relatively acidic metal hydrides such as  $\text{CpW}(\text{CO})_3\text{H}$  protonate the  $\beta$ -carbon of the alkynyl ligand, producing the cationic ruthenium vinylidene, with a metal anion as the counterion (eq 4). Opposite regiochemistry is indeed observed in the reaction



of metal alkynyl complexes with acidic vs hydridic metal hydrides, since the H from the hydridic zirconium hydride is delivered to the  $\alpha$ -carbon of the metal alkynyl complex, resulting in a 1,2-dimetalloalkene. Although the products from both of these reactions are those expected on the basis of the distinct reactivity characteristics of the two different classes of metal hydrides, these reactivity patterns are not indicative of mechanistic details for formation of the two products. In particular, while the reaction of  $\text{CpW}(\text{CO})_3\text{H}$  with  $\text{Cp}(\text{PMe}_3)_2\text{RuC}\equiv\text{CCH}_3$  involves proton transfer, the opposite regiochemistry observed in the reaction of the same alkynyl complex with  $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]_n$  does not require that this reaction involve direct hydride transfer. The formation of **2** results from a formal insertion of the  $\text{C}\equiv\text{C}$  bond into the  $\text{Zr}-\text{H}$  bond. The use of hydrozirconation reactions of  $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]_n$  with organic alkynes and olefins is well-established in organic chemistry,<sup>36</sup> and the *cis* insertion of  $\text{Zr}-\text{H}$  found here in the formation of the dimetalloalkenes is analogous to the stereochemistry found for reactions of other alkynes with  $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]_n$ . In contrast, insertion of electron-deficient alkynes such as  $\text{CH}_3\text{O}_2\text{C}\equiv\text{CCO}_2\text{CH}_3$  into the  $\text{M}-\text{H}$  bond of  $\text{Cp}_2\text{ReH}$ ,<sup>37</sup>  $\text{Cp}_2\text{WH}_2$ ,<sup>37</sup>  $\text{Cp}_2\text{NbH}(\text{CO})$ ,<sup>38</sup> *trans*- $\text{H}_2\text{Pt}(\text{PCy}_3)_2$ ,<sup>39</sup> or  $\text{Cp}^*\text{Rh}(\text{PMe}_3)\text{H}(\text{Ph})$ <sup>40</sup> gives either *trans* only or a mixture of *cis* and *trans* insertion products. In the case of  $\text{Cp}_2\text{ReH}$  and  $\text{Cp}_2\text{WH}_2$ , Herberich and Barlage showed<sup>37</sup> that the *trans* insertion products were the kinetic products, and that a subsequent isomerization

led to *cis* products. These reactions have been proposed to proceed by a mechanism involving electron transfer followed by proton transfer and radical combination. This mechanism is quite distinct from that for formation of *cis* products from electronically unsaturated metal hydrides such as  $[\text{Cp}_2\text{Zr}(\text{H})\text{Cl}]_n$  and  $\text{Cp}^*\text{ZrH}_2$ ,<sup>41</sup> which involves coordination of alkyne to the metal, followed by insertion into the  $\text{Zr}-\text{H}$  bond.

**Structure of  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{CHZrClCp}_2$  and Comparison with Other Dimetalloalkenes.** There is considerable diversity in the ways in which an RCCR moiety can bridge two metals. The bridging acetylene complexes of type D have their  $\text{M}-\text{M}$  bond oriented perpendicular to the  $\text{C}-\text{C}$  bond. Well-known acetylene complexes of this type include numerous compounds of general formula  $\text{Co}_2(\text{CO})_6(\text{RCCR}')$ .<sup>42</sup> The dimetalloalkene complexes of type E<sup>43</sup> can have the same overall formula as the bridging acetylene complexes of type D,<sup>43</sup> but the type E<sup>43</sup> complexes have a parallel orientation of the  $\text{M}-\text{M}$  bond relative to the  $\text{C}-\text{C}$  bond.



The general drawing E depicts a dimetalloalkene, which has a metal-metal bond. Examples of type F<sup>43</sup> are also known, where the two metals in the dimetalloalkene are *cis* to each other, but no metal-metal bond is present. In addition to the structural differences, a molecular orbital analysis<sup>44</sup> by Hoffman and co-workers indicates that complexes of type D are quite different electronically from those of type E or F. There are substantial differences in the Ru/Zr dimetalloalkene complexes reported in this paper (of general type G) compared to the dimetalloalkenes of type E or F. The two metals are *cis* to each other in E and F but *trans* in G. Another difference in the complexes of types E and F and those reported in this paper is that most of the complexes of type E and F have electron-withdrawing substituents (R) bonded to carbon; in many cases, the synthesis of these complexes involves addition of an electron-deficient alkyne such as  $\text{CF}_3\text{C}\equiv\text{CCF}_3$  or  $\text{CH}_3\text{O}_2\text{C}\equiv\text{CCO}_2\text{CH}_3$  to a bimetallic complex. Finally, nearly all of the examples of each of these types of complexes have identical metals as opposed to the early and late metal combination of the  $\text{RuCH}=\text{CHZr}$  complex **2**.

Dimetalloalkene complexes containing two different metals are rare, but our structural results for **2** can be compared with two homometallic dimetalloalkenes, one of which contains the same Zr fragment  $[\text{Cp}_2\text{ZrCl}]$ , and the other the same Ru fragment  $[\text{Cp}(\text{PMe}_3)_2\text{Ru}]$ , as found in **2**. Beck and co-workers have developed a method for synthesis of a variety of hydrocarbon-bridged bimetallic compounds by reaction of a metal carbonyl anion with cationic complexes containing  $\pi$ -bonded unsaturated hydrocarbons.<sup>45</sup> With use of this methodology, the reaction of  $\text{CpRu}(\text{CO})_2^-$  with  $[\text{Cp}(\text{PMe}_3)_2\text{Ru}(\eta^2-\text{CH}_3\text{O}_2\text{C}\equiv\text{CCO}_2\text{CH}_3)]^+$  led to the isolation of the dimetalloalkene complex **7**.<sup>46</sup> Note that although the two metals in **7** are the same, the ligands on Ru are different so that it resembles **2** not only in having a  $\text{Cp}(\text{PMe}_3)_2\text{Ru}$  moiety at one end of the molecule, but also in having one metal

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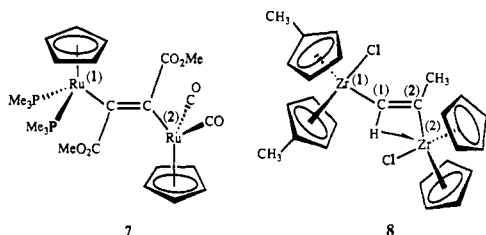
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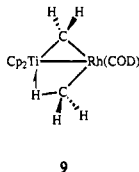




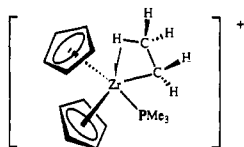
center being substantially more electron-rich than the other. The Ru(1)–C distance of 2.148 (3) Å in **7** is slightly longer than the Ru–C distance of 2.095 (16) Å found for **2**. The Ru(1)–C–C angle of 130.5 (2)° in the Ru<sub>2</sub> complex **7** is smaller than the Ru–C–C angle of 144 (1)° found in **2**.

The synthetic method used in Scheme I for the synthesis of our Ru/Zr dimetalloalkene **2** follows that utilized earlier by Erker and co-workers<sup>47</sup> in the synthesis of the Zr/Zr dimetalloalkene **8** from the reaction of (CH<sub>3</sub>C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>(Cl)ZrC≡CCH<sub>3</sub> with [Cp<sub>2</sub>Zr(H)Cl]<sub>n</sub>. The Zr(2)–C(2) distance of 2.209 (4) Å in their Zr/Zr complex **8** is comparable to the Zr–C distance of 2.185 (19) Å in **2**. Other bond distances pertinent to the agostic interaction in **2** include the Zr–C(2) distance of 2.564 (17) Å and the Zr–H distance of 2.08 (2) Å. Both of these are similar to analogous distances in Erker's dimetalloalkene **8**.

**Structure of Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH<sub>2</sub>CH<sub>2</sub>ZrClCp<sub>2</sub> and Comparison with Other Dimetalloalkanes.** Several complexes have been prepared in which early and late metals are linked by a –CH<sub>2</sub>–bridge.<sup>3,4</sup> Grubbs and co-workers have prepared complexes that exhibit agostic interactions between the CH on a bridging ligand and the early transition metal.<sup>3</sup> One of their compounds that is related to the Ru/Zr dimetalloalkane complex **1** reported in this paper is their Ti/Rh complex **9**, which contains two C<sub>1</sub> bridges, a normal methylene bridge and a bridging agostic methyl group.<sup>3b</sup>



The acute Zr–C–C angle of 82.5 (6)° found in the structure of **1** is smaller than the Zr–C–C angle of 91 (1)° in **2**. Both of these represent a roughly equivalent contraction of ~27° in the Zr–C–C angle (from the idealized 109° angle for the sp<sup>3</sup> carbon in **1**, and the idealized 120° angle for the sp<sup>2</sup> carbon in **2**). Acute M–C–C angles found in mononuclear complexes exhibiting agostic interactions with a C–H that is β to the metal include the Ti–C–C angle of 86.3 (6)° found<sup>48</sup> in (Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>)Cl<sub>2</sub>TiCH<sub>2</sub>CH<sub>3</sub> and the Co–C–C angle of 74.5 (2)° determined<sup>49</sup> for [P(*p*-tolyl)<sub>3</sub>(C<sub>5</sub>Me<sub>5</sub>)CoCH<sub>2</sub>CH<sub>3</sub>]<sup>+</sup>. Of more direct relevance to the zirconium complexes reported herein is the cationic zirconium complex [(C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)Zr(CH<sub>2</sub>CH<sub>3</sub>)]<sup>+</sup> reported by Jordan and co-workers,<sup>50</sup> which exhibits a Zr–C–C angle of 84.7 (5)°. The Zr–H distance of 2.19 (2) Å found for **1** is equal within experimental uncertainty to the Zr–H distance of 2.16 Å found in [(C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)Zr(CH<sub>2</sub>CH<sub>3</sub>)]<sup>+</sup>. The distance between



Zr and the β-carbon is smaller in **1** (2.549 (9) Å) compared to that found in [(C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)Zr(CH<sub>2</sub>CH<sub>3</sub>)]<sup>+</sup> (2.629 (9) Å). Despite these similarities in bond distances and angles, a notable difference in these two zirconocene complexes is the location of the agostic interaction relative to the other two ligands in the bent sandwich structure. While the agostic CH occupies a central site (between the Cl and CH<sub>2</sub>CH<sub>2</sub>Ru ligands) in **1**, the agostic CH of the ethyl group in [(C<sub>5</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>2</sub>(PMe<sub>3</sub>)Zr(CH<sub>2</sub>CH<sub>3</sub>)]<sup>+</sup> resides at the lateral site.

The acute Zr–C–C angles and small distances between the Zr and the β-carbon observed in the compounds discussed above are reminiscent of structural features that were observed earlier in Et<sub>3</sub>Al–Cl(Cp)<sub>2</sub>ZrCH<sub>2</sub>CH<sub>2</sub>Zr(Cp)<sub>2</sub>Cl–AlEt<sub>3</sub> (**10**), which was synthesized and structurally characterized by Kaminsky and co-workers.<sup>51</sup> The Zr–C–C angle of 75.9° found in **10** is smaller than those found in any of the Zr complexes discussed above; the Zr–C<sub>α</sub> bond (2.36 Å) of **10** is longer than that found (2.276 (10) Å) in **1**, while the distance from Zr to the β-carbon in **10** (2.49 Å) is shorter than that (2.549 (9) Å) determined in **1**. It is possible that one CH bond of each CH<sub>2</sub> moiety in **10** is involved in an agostic interaction with a β-Zr atom, thus causing the acute Zr–C–C angles.

**NMR Evidence for the Agostic Interaction in **1** and **2**.** Along with the structural data that provided evidence for the β-CH agostic interaction in the solid state, an evaluation of diagnostic NMR and IR spectroscopic features indicates the presence of this interaction in solution. Erker and co-workers reported synthetic, spectroscopic, structural, and theoretical studies on mononuclear Cp<sub>2</sub>Zr(Cl)(alkenyl) complexes, several of which exhibit agostic interactions between Zr and a CH that is β to Zr.<sup>52</sup> Their calculations indicate that both steric and electronic effects are responsible for the observation of agostic interactions. Comparison of <sup>1</sup>H and <sup>13</sup>C NMR data for a series of Cp<sub>2</sub>Zr(X)CR=CHR complexes enabled them to deduce spectroscopic features that distinguish those which exhibited β-CH agostic interactions from those which had no agostic interaction.<sup>52a</sup> Diagnostic spectroscopic features that they noted for the ZrC<sub>α</sub>R=C<sub>β</sub>(H)R moiety included low-field <sup>1</sup>H NMR resonances for the agostic H, low-field <sup>13</sup>C NMR resonance for C<sub>α</sub>, and a large (~80–90 ppm) difference in <sup>13</sup>C NMR resonances for C<sub>α</sub> compared to C<sub>β</sub>. With use of their criteria,<sup>52a</sup> it is clear that the low-field <sup>1</sup>H NMR resonance (δ 9.46) of the agostic CH of **2**, as well as the <sup>13</sup>C NMR chemical shifts of both of the bridging carbons in **2**, is suggestive of an agostic interaction.

A widely applied criterion<sup>8</sup> for assignment of an agostic interaction is the diminished C–H coupling constant that results from the reduced C–H bond order in the three-center, two-electron agostic interaction. The <sup>1</sup>J<sub>CH</sub> value of 110 Hz for the RuCH in **2** and that of 111 Hz in **1** are indicative of agostic interactions, and are similar to those seen in other alkyl<sup>50</sup> and alkenyl<sup>52a</sup> Zr complexes with β-CH agostic interactions. The fact that the <sup>1</sup>J<sub>CH</sub> values are essentially the same in **2** and **1** reflects the fact that the observed value is a direct measure of <sup>1</sup>J<sub>CH</sub> in **2** but is an averaged value of rapidly exchanging terminal and agostic β-CH<sub>2</sub> hydrogens in **1**.

Although a low <sup>1</sup>J<sub>CH</sub> has been commonly used to identify agostic structures by NMR, there is some evidence that <sup>1</sup>J<sub>CH</sub> values from the α-CH can also be useful in cases where a β-CH is suspected to be agostic. In their study of Cp\*<sub>2</sub>ScEt (which is thought to have a β-CH agostic interaction) and related compounds, Bercaw and co-workers suggested that "an abnormally large <sup>13</sup>C<sub>α,H</sub> coupling constant may signal a β agostic structure."<sup>53</sup> While additional data from a larger set of compounds would be useful in

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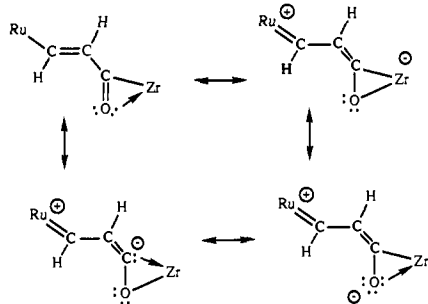


Figure 5. Resonance forms of 2-CO.

determining the generality of this trend, our data are supportive of this pattern. The  $^1J_{\text{CH}} = 157$  Hz found for the ZrCH of **2** is significantly larger than the values of  $^1J_{\text{CH}} = 115$ – $131$  Hz for several  $\text{Cp}_2\text{Zr}(\text{X})\text{CR}=\text{CHR}$  complexes that do not exhibit agostic interactions.<sup>52</sup> Similarly, the  $^1J_{\text{CH}} = 145$  Hz measured for the ZrCH of **1** exceeds the value expected in the absence of a  $\beta$ -agostic interaction. Similar  $^1J_{\text{C}_\alpha\text{H}}$  values were also found in other early metal complexes exhibiting  $\beta$ -agostic interactions,  $(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)\text{Cl}_3\text{TiCH}_2\text{CH}_3$ <sup>48</sup> and  $[(\text{C}_3\text{H}_4\text{CH}_3)_2(\text{PMe}_3)\text{Zr}(\text{CH}_2\text{CH}_3)]^+$ .<sup>50</sup>

A  $\beta$ -hydride elimination reaction of **1** is readily observed<sup>54</sup> under conditions where the initially formed mononuclear product  $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$  is trapped by alkynes or other reagents. This reaction results in reversion to the starting materials from which **1** was prepared,  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{CH}_2$  and  $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ . To the extent that the  $\beta$ -agostic interaction provides a model for a point along the reaction coordinate for  $\beta$ -hydride elimination, the structure of **1** should reflect partial C=C bond character. Accordingly, the C–C length of 1.485 (14) Å is shorter than an average organic C–C bond length<sup>26</sup> of about 1.52 Å. This partial C=C bond character would, in turn, account for the  $^1J_{\text{CH}}$  being larger than expected.

**Comparison of  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{CHC}(\text{O})\text{ZrClCp}_2$  with Related Complexes.** Carbonylation of the dimetalloalkene complex **2** gives the  $\eta^2$ -acyl complex 2-CO. While the formation of acyl complexes from carbonylation of metal–vinyl bonds is less common than the analogous reaction with metal–alkyl bonds, it has been previously observed for other zirconocene vinyl complexes. Erker and co-workers<sup>55</sup> have recently reported the characterization of the  $\eta^2$ -acyl complex **11**, which results from carbonylation of  $(\text{MeC}_3\text{H}_4)_2\text{Zr}(\text{Cl})(\text{CH}=\text{CHSiMe}_3)$ . The  $\nu(\text{C}=\text{O})$  band of 2-CO at  $1443\text{ cm}^{-1}$  appears at a considerably lower frequency than that of **11** at  $1511\text{ cm}^{-1}$ , which is similar to those seen in other zirconocene acyls.<sup>11</sup> This and other spectroscopic and structural data suggest that zwitterionic resonance forms are essential contributors to the electronic structure of 2-CO. The zwitterionic resonance form shown in eq 3 is actually a composite representing three zwitterionic resonance forms shown along with the neutral resonance form in Figure 5. Grubbs and co-workers have reported<sup>56</sup> the structure of the enolate anion  $[\text{Cp}_2\text{Zr}(\eta^2\text{-OC}=\text{CH}_2)\text{-CH}_3]^- \text{Na}^+ \cdot 2\text{THF}$ , **12**. The acyl complex **11** is similar to the expected structure of the neutral resonance form of 2-CO, while the bonding of **12** closely mimics that proposed for the zwitterionic resonance form of 2-CO. Since excellent models for each of the two different types of resonance forms of our acyl complex have been structurally characterized, it presents an opportunity for detailed structural comparison (Figure 6, with the zwitterionic resonance form of 2-CO shown). The Zr–O bond length of 2-CO is very similar to that found in **12**, and is much shorter than that in **11**. The C–O and C(1)–C(2) bond lengths of 2-CO are intermediate between analogous bond lengths in **11** and **12**. The Ru–C(3) bond length is essentially equal to those found in two other complexes in which a combination of neutral and zwitterionic

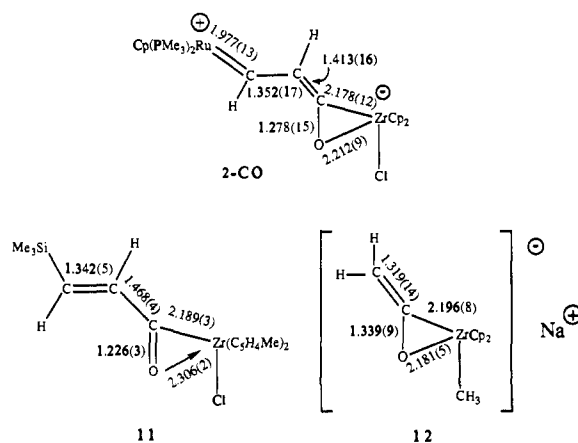
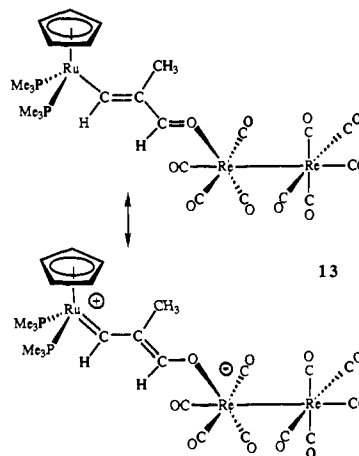


Figure 6. Comparison of the bond lengths of 2-CO (zwitterionic resonance form shown here) with bond lengths of two related zirconium complexes.

resonance forms (and a Ru–C bond order between 1 and 2) are proposed—the dimetalloalkyne **3** reported in this paper and the previously reported<sup>57</sup> RuRe<sub>2</sub> complex **13**, which has a Ru–C bond length of 1.986 (9) Å. On the basis of the spectroscopic and structural data, we believe that both the neutral and zwitterionic resonance forms of 2-CO contribute substantially to the overall electronic structure.



## Summary and Conclusion

A series of Ru/Zr complexes have been prepared in which an electron-rich metal [ $\text{Cp}(\text{PMe}_3)_2\text{Ru}$ ] is linked to an electron-deficient metal [ $\text{Cp}_2\text{ClZr}$ ] by  $\text{C}_2$  bridges in which the two carbons have formal bond orders of 3, 2, and 1. All three of these complexes, which contain  $\text{RuC}\equiv\text{CZr}$ ,  $\text{RuCH}=\text{CHZr}$ , and  $\text{RuCH}_2\text{CH}_2\text{Zr}$  moieties, have been fully characterized by spectroscopic measurements and single-crystal X-ray diffraction. This is the first homologous series in which two different metals linked by  $\text{C}_2$  bridges of all three bond orders have been synthesized and fully characterized. In the  $\text{RuCH}=\text{CHZr}$  and  $\text{RuCH}_2\text{CH}_2\text{Zr}$  complexes, spectroscopic and structural data indicate a  $\beta$ -agostic interaction between the Zr center and the CH adjacent to Ru. The differences in electronic properties of the two metals lead to a substantial contribution from zwitterionic resonance forms in the  $\eta^2$ -acyl complex resulting from insertion of CO into the Zr–C bond of  $\text{Cp}(\text{PMe}_3)_2\text{RuCH}=\text{CHZrClCp}_2$ .

## Experimental Section

**General Procedures.** All manipulations of oxygen- or water-sensitive compounds were carried out under an atmosphere of argon by using Schlenk or vacuum-line techniques, or in a Vacuum Atmospheres drybox. Glassware was dried in a  $120\text{ }^\circ\text{C}$  oven for several hours, or was flame-

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dried and cooled under vacuum immediately prior to use. <sup>1</sup>H (300 MHz) and <sup>13</sup>C NMR (75 MHz) spectra were recorded on a Bruker AM-300 spectrometer. <sup>13</sup>C NMR spectra were recorded in the presence of Cr(acac)<sub>3</sub> (0.04–0.07 M). <sup>1</sup>J<sub>CH</sub> coupling constants were obtained from <sup>13</sup>C NMR spectra by using gated decoupling. The PMe<sub>3</sub> resonances in these compounds do not appear as a simple first-order pattern in the NMR. In the <sup>1</sup>H NMR, the PMe<sub>3</sub> resonances appear as a A<sub>9</sub>XX'A<sub>9</sub> pattern; the appearance of these resonances in the <sup>1</sup>H NMR is a "filled-in doublet", with the separation of the outer lines being equal to <sup>2</sup>J<sub>PH</sub> + <sup>4</sup>J<sub>PH</sub>.<sup>58</sup> In the <sup>13</sup>C{<sup>1</sup>H} NMR, the PMe<sub>3</sub> resonance appears as a virtual triplet (designated as vt in the spectral assignments below); the observed coupling constant *J* is equal to <sup>1</sup>J<sub>PC</sub> + <sup>3</sup>J<sub>PC</sub>.<sup>58</sup> The <sup>1</sup>H chemical shifts were referenced to the residual proton peak of the solvent: C<sub>6</sub>D<sub>6</sub>H, δ 7.15; CHDCl<sub>2</sub>, δ 5.32; and CHD<sub>2</sub>CN, δ 1.93. The <sup>13</sup>C chemical shifts were referenced to the central peak of CD<sub>2</sub>Cl<sub>2</sub> (δ 53.8) or C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> (CD<sub>3</sub> at δ 20.4). IR spectra were recorded on a Mattson Polaris FT-IR spectrometer. Elemental analyses were carried out by Schwarzkopf Micro-analytical Laboratory or by Galbraith Laboratory.

**Materials.** THF was distilled from Na/benzophenone. Toluene and hexanes were stirred over concentrated H<sub>2</sub>SO<sub>4</sub> until the H<sub>2</sub>SO<sub>4</sub> remained colorless; these solvents were then distilled from Na/benzophenone and stored over [Cp<sub>2</sub>TiCl<sub>2</sub>]<sub>2</sub>ZnCl<sub>2</sub>.<sup>59</sup> Dichloromethane was distilled from P<sub>2</sub>O<sub>5</sub>. Anhydrous diethyl ether was stored over [Cp<sub>2</sub>TiCl<sub>2</sub>]<sub>2</sub>ZnCl<sub>2</sub> and vacuum transferred immediately prior to use. Benzene-*d*<sub>6</sub> was dried over NaK and stored over [Cp<sub>2</sub>TiCl<sub>2</sub>]<sub>2</sub>ZnCl<sub>2</sub>. Dichloromethane-*d*<sub>2</sub> was dried over P<sub>2</sub>O<sub>5</sub> and stored over CaH<sub>2</sub>. THF-*d*<sub>8</sub> was dried and stored over NaK. Acetonitrile-*d*<sub>3</sub> was dried over activated 3-Å sieves and stored over Cp<sub>2</sub>Zr(Me)Cl. Cp<sub>2</sub>Zr(Me)Cl,<sup>60</sup> Cp<sub>2</sub>Zr(D)Cl,<sup>10,61</sup> and Cp<sub>2</sub>Zr(NMe<sub>2</sub>)<sub>2</sub><sup>62</sup> were prepared according to literature procedures. [Cp<sub>2</sub>Zr(H)Cl]<sub>n</sub> was obtained from Aldrich and used as received, or prepared according to a literature procedure.<sup>61</sup> Carbon monoxide (Matheson), (trimethylsilyl)acetylene (Fluka), propyne (Farchan), PMe<sub>3</sub> (Strem), Me<sub>3</sub>SnNMe<sub>2</sub> (Aldrich), and Cp<sub>2</sub>ZrCl<sub>2</sub> (Boulder Scientific) were used as received. NH<sub>4</sub>PF<sub>6</sub> (Aldrich) was dried at 100 °C under vacuum. KO<sup>t</sup>Bu (Aldrich) was purified by sublimation (120 °C, 10<sup>-4</sup> mmHg). Cp(PMe<sub>3</sub>)<sub>2</sub>RuCl was prepared by a modification of previously reported procedures.<sup>63</sup> Severe face rashes were recently reported<sup>64</sup> to result from exposure to Cp(PMe<sub>3</sub>)<sub>2</sub>RuCl, so adequate precautions should be taken.

[Cp(PMe<sub>3</sub>)<sub>2</sub>Ru=C=CH<sub>2</sub>][PF<sub>6</sub>]. A complex originally thought<sup>65</sup> to be [Cp(PMe<sub>3</sub>)<sub>2</sub>Ru=C=CH<sub>2</sub>][PF<sub>6</sub>] was later determined<sup>6</sup> to be the η<sup>2</sup>-acetylene isomer [Cp(PMe<sub>3</sub>)<sub>2</sub>Ru(η<sup>2</sup>-HC≡CH)][PF<sub>6</sub>]. The following procedure is a convenient preparation of authentic [Cp(PMe<sub>3</sub>)<sub>2</sub>Ru=C=CH<sub>2</sub>][PF<sub>6</sub>]. MeOH (40 mL) was added by vacuum transfer to a flask charged with Cp(PMe<sub>3</sub>)<sub>2</sub>RuCl (810 mg, 2.29 mmol) and NH<sub>4</sub>PF<sub>6</sub> (3.29 g, 20.2 mmol). After the solids had dissolved, Me<sub>3</sub>SiC≡CH (1.29 mL, 9.16 mmol) was added by syringe. The reaction was stirred for 1 h, during which time a yellow precipitate formed. The slurry was concentrated, and the yellow solid was isolated by filtration (in the air). The yellow solid was washed with H<sub>2</sub>O, MeOH, and Et<sub>2</sub>O and then dried under vacuum to give a bright yellow solid (920 mg, 82%). Typical yields were 70–85%. <sup>1</sup>H NMR (CD<sub>3</sub>CN): δ 5.43 (s, 5 H, Cp), 3.78 (t, <sup>4</sup>J<sub>PH</sub> = 2.4 Hz, 2 H, CH<sub>2</sub>), 1.57 (filled-in doublet, <sup>2</sup>J<sub>PH</sub> + <sup>4</sup>J<sub>PH</sub> = 10.4 Hz, 18 H, PMe<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 0.05 M Cr(acac)<sub>3</sub>): δ 343.7 (t, <sup>2</sup>J<sub>PC</sub> = 16 Hz, Ru=C), 92.7 (t, <sup>1</sup>J<sub>CH</sub> = 163 Hz, CH<sub>2</sub>), 92.0 (d, <sup>1</sup>J<sub>CH</sub> = 179 Hz, Cp), 22.3 (q of vt, <sup>1</sup>J<sub>CH</sub> = 132 Hz, <sup>2</sup>J<sub>PC</sub> + <sup>4</sup>J<sub>PC</sub> = 37 Hz, PMe<sub>3</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(C=C) 1633 cm<sup>-1</sup>. Anal. Calcd for C<sub>13</sub>H<sub>25</sub>F<sub>6</sub>P<sub>3</sub>Ru: C, 31.91; H, 5.16. Found: C, 31.94; H, 5.26.

[Cp(PMe<sub>3</sub>)<sub>2</sub>Ru=C=C(H)Me][PF<sub>6</sub>]. This complex was prepared by a minor modification of the literature procedure.<sup>65</sup> In analogy to the preparation of [Cp(PMe<sub>3</sub>)<sub>2</sub>Ru=C=CH<sub>2</sub>][PF<sub>6</sub>] described above, MeC≡CH was bubbled through a MeOH solution containing Cp(PMe<sub>3</sub>)<sub>2</sub>RuCl and NH<sub>4</sub>PF<sub>6</sub> for 1 h, followed by stirring of the solution under a MeC≡CH atmosphere overnight. Workup as described above produced an orange-yellow solid (yield 75–95%). <sup>1</sup>H NMR (CD<sub>3</sub>CN):

δ 5.41 (s, 5 H, Cp), 4.31 (qt, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, <sup>4</sup>J<sub>PH</sub> = 2.2 Hz, 1 H, CH), 1.77 (dt, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, <sup>5</sup>J<sub>PH</sub> = 0.7 Hz, 3 H, Me), 1.55 (filled-in doublet, <sup>2</sup>J<sub>PH</sub> + <sup>4</sup>J<sub>PH</sub> = 10.3 Hz, 18 H, PMe<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>3</sub>CN, 0.05 M Cr(acac)<sub>3</sub>): δ 347.6 (t, <sup>2</sup>J<sub>PC</sub> = 16 Hz, Ru=C), 103.3 (d, <sup>1</sup>J<sub>CH</sub> = 155 Hz, Ru=C=C), 91.7 (d, <sup>1</sup>J<sub>CH</sub> = 179 Hz, Cp), 22.9 (q of vt, <sup>1</sup>J<sub>CH</sub> = 130 Hz, <sup>1</sup>J<sub>PC</sub> + <sup>3</sup>J<sub>PC</sub> = 37 Hz, PMe<sub>3</sub>), 4.5 (q, <sup>1</sup>J<sub>CH</sub> = 130 Hz, Me).

Cp(PMe<sub>3</sub>)<sub>2</sub>Ru=C=CH. THF (25 mL) was added by vacuum transfer to a flask charged with [Cp(PMe<sub>3</sub>)<sub>2</sub>Ru=C=CH<sub>2</sub>][PF<sub>6</sub>] (1.462 g, 2.99 mmol) and KO<sup>t</sup>Bu (0.370 g, 3.30 mmol) at -78 °C. The slurry was stirred at -78 °C for 1 h to give a green solution that turned yellow and formed a precipitate as it warmed to room temperature. (The reason for the transient green coloration is unknown, but it was reproducibly observed.) After an additional 1 h, the solution was evaporated to dryness. The yellow residue was extracted with hexanes and filtered. The yellow filtrate was evaporated, and the residue sublimed at 90 °C (<10<sup>-4</sup> mmHg) to produce a bright yellow solid (0.912 g, 89%). Typical yields were 80–95%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 4.61 (s, 5 H, Cp), 1.45 (filled-in doublet, <sup>2</sup>J<sub>PH</sub> + <sup>4</sup>J<sub>PH</sub> = 9.1 Hz, 18 H, PMe<sub>3</sub>), 1.39 (t, <sup>4</sup>J<sub>PH</sub> = 2.6 Hz, 1 H, CH). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 0.05 M Cr(acac)<sub>3</sub>): δ 108.1 (dt, <sup>2</sup>J<sub>CH</sub> = 38 Hz, <sup>2</sup>J<sub>PC</sub> = 26 Hz, RuC), 91.0 (d, <sup>1</sup>J<sub>CH</sub> = 221 Hz, CH), 80.8 (d, <sup>1</sup>J<sub>CH</sub> = 176 Hz, Cp), 23.0 (q of vt, <sup>1</sup>J<sub>CH</sub> = 129 Hz, <sup>1</sup>J<sub>PC</sub> + <sup>3</sup>J<sub>PC</sub> = 30 Hz, PMe<sub>3</sub>). IR (KBr): ν(CH) 3266, ν(C≡C) 1924 cm<sup>-1</sup>. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(CH) 3272, ν(C≡C) 1921 cm<sup>-1</sup>. Anal. Calcd for C<sub>13</sub>H<sub>24</sub>P<sub>2</sub>Ru: C, 45.47; H, 7.06. Found: C, 45.81; H, 7.16.

Cp(PMe<sub>3</sub>)<sub>2</sub>Ru=C=Me. Synthesis of this compound by phosphine exchange between PMe<sub>3</sub> and Cp(PPh<sub>3</sub>)<sub>2</sub>Ru=C=Me has been reported.<sup>65</sup> However, we have found the following procedure more reliable and convenient. Cp(PMe<sub>3</sub>)<sub>2</sub>Ru=C=Me was prepared from [Cp(PMe<sub>3</sub>)<sub>2</sub>Ru=C=C(H)Me][PF<sub>6</sub>] (864 mg, 1.72 mmol) and KO<sup>t</sup>Bu (212 mg, 1.89 mmol) in THF as described above for Cp(PMe<sub>3</sub>)<sub>2</sub>Ru=C=CH. The product was obtained as a yellow solid after sublimation, with yields typically in the 75–85% range. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 4.55 (s, 5 H, Cp), 2.30 (t, <sup>5</sup>J<sub>PH</sub> = 2.5 Hz, 3 H, CH<sub>3</sub>), 1.24 (filled-in doublet, <sup>2</sup>J<sub>PH</sub> + <sup>4</sup>J<sub>PH</sub> = 8.9 Hz, 18 H, PMe<sub>3</sub>).

Cp(PMe<sub>3</sub>)<sub>2</sub>Ru=C=CZrClCp<sub>2</sub>, 3. **Method A: Amine Elimination.** A mixture of Cp(PMe<sub>3</sub>)<sub>2</sub>Ru=C=CH (445 mg, 1.30 mmol), Cp<sub>2</sub>Zr(NMe<sub>2</sub>)<sub>2</sub> (185 mg, 0.66 mmol), Cp<sub>2</sub>ZrCl<sub>2</sub> (191 mg, 0.65 mmol), and toluene (2 mL) gave a yellow slurry that turned orange, and then red and homogeneous, upon heating to 100 °C. Solution aliquots were periodically examined by <sup>1</sup>H NMR to monitor the extent of reaction. After 5.5 days at 100 °C, the reaction was ~90% complete. Addition of hexane gave a precipitate that was isolated by filtration, washed with hexanes, and dried under vacuum to give an orange solid (436 mg, 56% yield, 98% pure by <sup>1</sup>H NMR). A second crop from toluene/hexanes produced 237 mg (30%, 85% pure by <sup>1</sup>H NMR). Analytically pure 3 was obtained from slow diffusion of Et<sub>2</sub>O into a toluene solution at -20 °C.

**Method B: Methane Elimination.** A mixture of Cp(PMe<sub>3</sub>)<sub>2</sub>Ru=C=CH (251 mg, 0.73 mmol), Cp<sub>2</sub>Zr(CH<sub>3</sub>)Cl (199 mg, 0.73 mmol), and toluene (2 mL) gave a brown slurry that became a dark red homogeneous solution when heated to 130 °C. The sample was periodically freeze-pump-thawed degassed to remove the methane byproduct. Solution aliquots were examined by <sup>1</sup>H NMR to check the extent of reaction. After 15 days at 130 °C, the solution was concentrated to initiate precipitation. The precipitate was isolated by filtration, washed with hexanes, and dried under vacuum to give an orange microcrystalline solid (114 mg, 26% yield, >90% pure by <sup>1</sup>H NMR). A second crop from toluene/hexanes produced an orange solid of lower purity (129 mg, 59% pure). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 6.22 (s, 10 H, ZrCp), 4.71 (s, 5 H, RuCp), 1.46 (filled-in doublet, <sup>2</sup>J<sub>PH</sub> + <sup>4</sup>J<sub>PH</sub> = 9.1 Hz, 18 H, PMe<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 0.04 M Cr(acac)<sub>3</sub>): δ 190.4 (s, ZrC), 178.3 (t, <sup>2</sup>J<sub>PC</sub> = 23 Hz, RuC), 111.7 (d, <sup>1</sup>J<sub>CH</sub> = 173 Hz, ZrCp), 81.9 (d, <sup>1</sup>J<sub>CH</sub> = 174 Hz, RuCp), 23.3 (q of vt, <sup>1</sup>J<sub>CH</sub> = 126 Hz, <sup>3</sup>J<sub>PC</sub> = 31 Hz, PMe<sub>3</sub>). IR: (KBr) ν(C≡C) 1868 cm<sup>-1</sup>. IR (CH<sub>2</sub>Cl<sub>2</sub>): ν(C≡C) 1872 cm<sup>-1</sup>. Anal. Calcd for C<sub>22</sub>H<sub>33</sub>ClP<sub>2</sub>Zr: C, 46.10; H, 5.56. Found: C, 46.30; H, 5.48. Vis(THF): λ<sub>max</sub> 418 nm (ε could not be reliably determined due to the extreme hydrolytic sensitivity of this complex). Crystals of 3 suitable for X-ray diffraction analysis were grown by slowly cooling a saturated toluene/hexane solution from 80 °C to room temperature.

Cp(PMe<sub>3</sub>)<sub>2</sub>Ru=C=CSnMe<sub>3</sub>. Toluene (1 mL) was added to a flask containing Cp(PMe<sub>3</sub>)<sub>2</sub>Ru=C=CH (580 mg, 1.69 mmol) and excess Me<sub>3</sub>SnNMe<sub>2</sub> (0.5 mL, 3.06 mmol). The solution was stirred for 4 days, after which time the <sup>1</sup>H NMR spectrum indicated complete reaction. The volatiles were removed under vacuum to give a dark brown-yellow solid (760 mg, 89% yield). Sublimation at 80 °C (<10<sup>-4</sup> mmHg) gave an analytically pure yellow solid. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 4.61 (s, 5 H, Cp), 1.45 (filled-in doublet, <sup>2</sup>J<sub>PH</sub> + <sup>4</sup>J<sub>PH</sub> = 9 Hz, 18 H, PMe<sub>3</sub>), 0.04 (s with <sup>117,119</sup>Sn satellites, <sup>2</sup>J<sub>SnH</sub> = 55, 58 Hz, 9 H, SnMe<sub>3</sub>). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, 0.06 M Cr(acac)<sub>3</sub>): δ 145.3 (t, <sup>2</sup>J<sub>PC</sub> = 24 Hz, RuC), 102.3 (s with <sup>117,119</sup>Sn satellites, <sup>1</sup>J<sub>SnC</sub> = 586, 614 Hz, SnC), 81.1 (d, <sup>1</sup>J<sub>CH</sub> = 174 Hz, Cp), 22.9 (q of vt, <sup>1</sup>J<sub>CH</sub> = 126 Hz, <sup>1</sup>J<sub>PC</sub> + <sup>3</sup>J<sub>PC</sub> = 30 Hz, PMe<sub>3</sub>), -6.85

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(q with  $^{117,119}\text{Sn}$  satellites,  $^1J_{\text{CH}} = 127$  Hz,  $^1J_{\text{SnH}} = 369, 386$  Hz,  $\text{SnMe}_3$ ). IR (KBr):  $\nu(\text{C}=\text{C})$  1919  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{16}\text{H}_{32}\text{P}_2\text{RuSn}$ : C, 37.96; H, 6.39. Found: C, 38.00; H, 6.34.

**Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CHZrClCp<sub>2</sub>, 2.** THF (25 mL) was added by vacuum transfer to a flask charged with Cp(PMe<sub>3</sub>)<sub>2</sub>RuC≡CH (319 mg, 0.93 mmol) and [Cp<sub>2</sub>Zr(H)Cl]<sub>n</sub> (264 mg, 1.02 mmol) at -78 °C. The reaction was allowed to warm to room temperature and was stirred until the yellow slurry became red and nearly homogeneous (~2 h). The solution was filtered and the filtrate concentrated until precipitation began. Et<sub>2</sub>O was added to complete the precipitation. The solid was collected by filtration, washed with Et<sub>2</sub>O and hexanes, and dried under vacuum to give a yellow solid (444 mg, 79% yield, 88% pure by <sup>1</sup>H NMR). Typical yields ranged from 70% to 90%, with purities ranging from 80% to 90%. Analytically pure **2** was obtained from slow diffusion of Et<sub>2</sub>O into a concentrated toluene solution at -20 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 9.46 (dt, <sup>3</sup>J<sub>HH</sub> = 18.8 Hz, <sup>3</sup>J<sub>PH</sub> = 4.3 Hz, 1 H, RuCH), 8.38 (dt, <sup>3</sup>J<sub>HH</sub> = 18.8 Hz, <sup>4</sup>J<sub>PH</sub> = 0.8 Hz, 1 H, ZrCH), 5.83 (s, 10 H, ZrCp), 4.60 (s, 5 H, RuCp), 1.36 (filled-in doublet, <sup>2</sup>J<sub>PH</sub> + <sup>4</sup>J<sub>PH</sub> = 8.6 Hz, 18 H, PMe<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 0.07 M Cr(acac)<sub>3</sub>): δ 198.7 (dt, <sup>1</sup>J<sub>CH</sub> = 157 Hz, <sup>3</sup>J<sub>PC</sub> = 4 Hz, ZrCH), 114.7 (dt, <sup>1</sup>J<sub>CH</sub> = 110 Hz, <sup>2</sup>J<sub>PC</sub> = 16 Hz, RuCH), 109.8 (d, <sup>1</sup>J<sub>CH</sub> = 172 Hz, ZrCp), 81.3 (d, <sup>1</sup>J<sub>CH</sub> = 173 Hz, RuCp), 23.5 (q of vt, <sup>1</sup>J<sub>CH</sub> = 129 Hz, <sup>1</sup>J<sub>PC</sub> + <sup>3</sup>J<sub>PC</sub> = 28 Hz, PMe<sub>3</sub>). IR (KBr): agostic  $\nu(\text{CH})$  broad band centered at 2590  $\text{cm}^{-1}$ ,  $\nu(\text{C}=\text{C})$  1476  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{23}\text{H}_{35}\text{ClP}_2\text{RuZr}$ : C, 45.94; H, 5.88. Found: C, 45.97; H, 5.89. Crystals of **2** suitable for X-ray diffraction were grown by slow cooling of a saturated THF solution from room temperature to -20 °C.

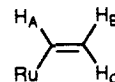
**Cp(PMe<sub>3</sub>)<sub>2</sub>RuCD=CHZrClCp<sub>2</sub>, 2-d<sub>1</sub>.** 2-d<sub>1</sub> was synthesized from Cp(PMe<sub>3</sub>)<sub>2</sub>RuC≡CH (79 mg, 0.23 mmol) and Cp<sub>2</sub>Zr(D)Cl (84 mg, 0.26 mmol) as described for **2**, in 90% yield (126 mg) with 85% purity (83% D). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 8.38 (t, <sup>3</sup>J<sub>HD</sub> = 2.7 Hz, 1 H, ZrCH), 5.83 (s, 10 H, ZrCp), 4.60 (s, 5 H, RuCp), 1.36 (filled-in doublet, <sup>2</sup>J<sub>PH</sub> + <sup>4</sup>J<sub>PH</sub> = 8.6 Hz, 18 H, PMe<sub>3</sub>). IR (KBr): agostic  $\nu(\text{CD})$  1900,  $\nu(\text{C}=\text{C})$  1465  $\text{cm}^{-1}$ .

**Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CMeZrClCp<sub>2</sub>.** Toluene (30 mL) was added by vacuum transfer to a flask containing Cp(PMe<sub>3</sub>)<sub>2</sub>RuC≡CMe (497 mg, 1.39 mmol) and [Cp<sub>2</sub>Zr(H)Cl]<sub>n</sub> (394 mg, 1.53 mmol) at -78 °C. After warming to room temperature, the yellow slurry was stirred overnight to give an orange homogeneous solution. The solvent was evaporated, and the residue was dissolved in THF and filtered. The THF filtrate was concentrated, and Et<sub>2</sub>O was added to initiate precipitation. The solid was collected by filtration, washed with Et<sub>2</sub>O and hexanes, and dried under vacuum to give a yellow solid (303 mg). A second crop from THF/hexanes produced 327 mg (73% total yield, 82% pure by <sup>1</sup>H NMR). Typical yields ranged from 70% to 90% with purities >80%. Analytically pure material was obtained by crystallization from toluene/hexanes at -20 °C. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 8.28 (tq, <sup>3</sup>J<sub>PH</sub> = 5.6 Hz, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz, 1 H, RuCH), 5.76 (s, 10 H, ZrCp), 4.50 (s, 5 H, RuCp), 2.26 (d, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz, 3 H, ZrCMe), 1.41 (filled-in doublet, <sup>2</sup>J<sub>PH</sub> + <sup>4</sup>J<sub>PH</sub> = 8.5 Hz, 18 H, PMe<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 0.05 M Cr(acac)<sub>3</sub>): δ 203.6 (t, <sup>3</sup>J<sub>PC</sub> = 4 Hz, ZrCMe), 109.7 (d, <sup>1</sup>J<sub>CH</sub> = 172 Hz, ZrCp), 96.3 (dt, <sup>1</sup>J<sub>CH</sub> = 116 Hz, <sup>2</sup>J<sub>PC</sub> = 15 Hz, RuCH), 79.9 (d, <sup>1</sup>J<sub>CH</sub> = 175 Hz, RuCp), 25.7 (s, ZrCMe, <sup>1</sup>J<sub>CH</sub> obscured by PMe<sub>3</sub> quartet), 24.0 (q of vt, <sup>1</sup>J<sub>CH</sub> = 122 Hz, <sup>1</sup>J<sub>PC</sub> + <sup>3</sup>J<sub>PC</sub> = 28 Hz, PMe<sub>3</sub>). IR (KBr): agostic  $\nu(\text{CH})$  2624 (br)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{24}\text{H}_{37}\text{ClP}_2\text{RuZr}$ : C, 46.85; H, 6.07. Found: C, 46.86; H, 6.12.

**Cp(PMe<sub>3</sub>)<sub>2</sub>RuCD=CMeZrClCp<sub>2</sub>.** Cp(PMe<sub>3</sub>)<sub>2</sub>RuCD=CMeZrClCp<sub>2</sub> was prepared from Cp(PMe<sub>3</sub>)<sub>2</sub>RuC≡CMe (140 mg, 0.39 mmol) and [Cp<sub>2</sub>Zr(D)Cl]<sub>n</sub> (114 mg, 0.44 mmol) in THF as described for **2**. This gave a yellow solid (168 mg, 70% yield, 90% purity, >95% D). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 5.76 (s, 10 H, ZrCp), 4.50 (s, 5 H, RuCp), 2.26 (s, 3 H, Me), 1.41 (filled-in doublet, <sup>2</sup>J<sub>PH</sub> + <sup>4</sup>J<sub>PH</sub> = 8.6 Hz, 18 H, PMe<sub>3</sub>). IR (KBr): agostic  $\nu(\text{CD})$  1914  $\text{cm}^{-1}$ .

**Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CH<sub>2</sub>.** The ruthenium vinyl complex can be prepared by the hydrolysis of isolated **2** or, more conveniently, by the hydrolysis of **2** prepared in situ. THF (25 mL) was added by vacuum transfer to a flask charged with Cp(PMe<sub>3</sub>)<sub>2</sub>RuC≡CH (317 mg, 0.92 mmol) and [Cp<sub>2</sub>Zr(H)Cl]<sub>n</sub> (262 mg, 1.02 mmol). The yellow slurry was stirred for 2-3 h at room temperature until it became dark red and homogeneous. Excess H<sub>2</sub>O (25  $\mu\text{L}$ , 1.39 mmol) was added by microliter syringe to give a yellow solution with a white precipitate. The reaction slurry was stirred for 45 min before the volatiles were evaporated under vacuum. The residue was extracted with hexanes. Removal of the volatiles from the hexane extract, followed by sublimation of the yellow residue at 45 °C (10<sup>-5</sup> mmHg) gave a waxy yellow solid (186 mg, 58% yield). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 7.46 (dxy, <sup>3</sup>J<sub>H<sub>A</sub>H<sub>C</sub></sub> = 18.1 Hz, <sup>3</sup>J<sub>H<sub>A</sub>H<sub>B</sub></sub> = 11.0 Hz, <sup>3</sup>J<sub>PH</sub> = 8.2 Hz, 1 H, H<sub>A</sub>), 5.78 (ddt, <sup>3</sup>J<sub>H<sub>A</sub>H<sub>B</sub></sub> = 11.0 Hz, <sup>2</sup>J<sub>H<sub>B</sub>H<sub>C</sub></sub> = 4.4 Hz, <sup>4</sup>J<sub>PH</sub> = 2.4 Hz, 1 H, H<sub>B</sub>), 5.12 (ddt, <sup>3</sup>J<sub>H<sub>A</sub>H<sub>C</sub></sub> = 18.1 Hz, <sup>2</sup>J<sub>H<sub>B</sub>H<sub>C</sub></sub> = 4.4 Hz, <sup>4</sup>J<sub>PH</sub> = 1.1 Hz, 1 H, H<sub>C</sub>), 4.50 (s, 5 H, Cp), 1.35 (filled-in doublet, <sup>2</sup>J<sub>PH</sub> + <sup>4</sup>J<sub>PH</sub> = 8.4 Hz, 18 H, PMe<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 0.04

M Cr(acac)<sub>3</sub>): δ 160.7 (dt, <sup>1</sup>J<sub>CH</sub> = 129 Hz, <sup>2</sup>J<sub>PC</sub> = 18 Hz, CH), 121.8 (tt, <sup>1</sup>J<sub>CH</sub> = 149 Hz, <sup>3</sup>J<sub>PC</sub> = 4 Hz, CH<sub>2</sub>), 81.7 (dt, <sup>1</sup>J<sub>CH</sub> = 174 Hz, <sup>2</sup>J<sub>PC</sub> = 2 Hz, Cp), 22.7 (q of vt, <sup>1</sup>J<sub>CH</sub> = 124 Hz, <sup>1</sup>J<sub>PC</sub> + <sup>3</sup>J<sub>PC</sub> = 28 Hz, PMe<sub>3</sub>). IR (KBr):  $\nu(\text{C}=\text{C})$  1531  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{13}\text{H}_{26}\text{P}_2\text{Ru}$ : C, 45.20; H, 7.60. Found: C, 45.89; H, 7.51.



Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CH<sub>2</sub> can also be prepared from the alcoholysis of **2**. A NMR sample of **2** in C<sub>6</sub>D<sub>6</sub> was treated with 1 equiv of ROH (R = Me, Et). The orange solution immediately turned yellow. <sup>1</sup>H NMR confirmed the quantitative formation of Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CH<sub>2</sub> and Cp<sub>2</sub>Zr(OR)Cl (R = Me, Et). However, in preparative reactions, Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CH<sub>2</sub> and Cp<sub>2</sub>Zr(OR)Cl could not be separated due to similar solubility and sublimation properties.

**Cp(PMe<sub>3</sub>)<sub>2</sub>RuCD=CH<sub>2</sub>.** Cp(PMe<sub>3</sub>)<sub>2</sub>RuCD=CH<sub>2</sub> was prepared by the hydrolysis of 2-d<sub>1</sub> which was prepared in situ from Cp(PMe<sub>3</sub>)<sub>2</sub>RuC≡CH (128 mg, 0.37 mmol) and [Cp<sub>2</sub>Zr(D)Cl]<sub>n</sub> (108 mg, 0.42 mmol), as described for Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CH<sub>2</sub>, in 65% yield (83 mg) and 91% D. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 5.81 (br m, 1 H, H<sub>B</sub>), 5.17 (br m, 1 H, H<sub>C</sub>), 4.53 (s, 5 H, Cp), 1.34 (filled-in doublet, <sup>2</sup>J<sub>PH</sub> + <sup>4</sup>J<sub>PH</sub> = 8.4 Hz, 18 H, PMe<sub>3</sub>).

**Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH<sub>2</sub>CH<sub>2</sub>ZrClCp<sub>2</sub>, 1.** THF (25 mL) was added by vacuum transfer to a flask charged with Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CH<sub>2</sub> (396 mg, 1.15 mmol) and [Cp<sub>2</sub>Zr(H)Cl]<sub>n</sub> (325 mg, 1.26 mmol). The yellow slurry was stirred for 2-3 h until it became red and homogeneous. The THF solution was filtered and concentrated, and then Et<sub>2</sub>O was added to initiate precipitation. The precipitate was collected by filtration, washed with Et<sub>2</sub>O and hexanes, and dried under vacuum to give an orange solid (492 mg, 71% yield, 89% purity by <sup>1</sup>H NMR). Slow diffusion of hexanes into a concentrated toluene solution produced analytically pure **1**. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 5.76 (s, 10 H, ZrCp), 4.40 (s, 5 H, RuCp), 1.56 (m, 2 H, ZrCH<sub>2</sub>), 1.40 (filled-in doublet, <sup>2</sup>J<sub>PH</sub> + <sup>4</sup>J<sub>PH</sub> = 8.5 Hz, 18 H, PMe<sub>3</sub>), -0.29 (m, 2 H, RuCH<sub>2</sub>). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 5.76 (s, 10 H, ZrCp), 4.30 (s, 5 H, RuCp), 1.39 (m, 2 H, ZrCH<sub>2</sub>), 1.16 (filled-in doublet, <sup>2</sup>J<sub>PH</sub> + <sup>4</sup>J<sub>PH</sub> = 8.4 Hz, 18 H, PMe<sub>3</sub>), -0.05 (m, 2 H, RuCH<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 0.05 M Cr(acac)<sub>3</sub>): δ 106.9 (s, ZrCp), 79.3 (s, RuCp), 22.6 (vt, <sup>1</sup>J<sub>PC</sub> + <sup>3</sup>J<sub>PC</sub> = 26 Hz, PMe<sub>3</sub>), -36.3 (t, <sup>1</sup>J<sub>PC</sub> = 8 Hz, RuCH<sub>2</sub>). The ZrCH<sub>2</sub> resonance was obscured by the solvent resonance in CD<sub>2</sub>Cl<sub>2</sub> but was observed in toluene-d<sub>8</sub>. <sup>13</sup>C NMR (toluene-d<sub>8</sub> at 220 K, 0.06 M Cr(acac)<sub>3</sub>): δ 107.7 (d, <sup>1</sup>J<sub>CH</sub> = 172 Hz, ZrCp), 80.0 (d, <sup>1</sup>J<sub>CH</sub> = 174 Hz, RuCp), 53.9 (br t, <sup>1</sup>J<sub>CH</sub> = 145 Hz, ZrCH<sub>2</sub>), PMe<sub>3</sub> resonance was obscured by CD<sub>3</sub> resonance of solvent, -34.5 (t, <sup>1</sup>J<sub>CH</sub> = 111 Hz, <sup>1</sup>J<sub>PC</sub> not well-resolved, RuCH<sub>2</sub>). IR (KBr):  $\nu(\text{agostic CH})$  2743  $\text{cm}^{-1}$ . UV-vis (toluene):  $\lambda_{\text{max}}$  342 nm ( $\epsilon = 7.1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ), 422 ( $\epsilon = 3.6 \times 10^3$ ). Anal. Calcd for  $\text{C}_{23}\text{H}_{37}\text{ClP}_2\text{RuZr}$ : C, 45.79; H, 6.19. Found: C, 45.37; H, 6.27. Crystals of **1** suitable for X-ray diffraction analysis were grown by cooling a saturated toluene solution from room temperature to -20 °C.

**Cp(PMe<sub>3</sub>)<sub>2</sub>RuCHDCH<sub>2</sub>ZrClCp<sub>2</sub>, 1-d<sub>1</sub>.** 1-d<sub>1</sub> was prepared from Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CH<sub>2</sub> (143 mg, 0.41 mmol) and [Cp<sub>2</sub>Zr(D)Cl]<sub>n</sub> (150 mg, 0.46 mmol) in THF as described for **1**. This gave an orange solid (187 mg, 75% yield, 80% purity, and 80% D). 1-d<sub>1</sub> can be similarly prepared from Cp(PMe<sub>3</sub>)<sub>2</sub>RuCD=CH<sub>2</sub> and [Cp<sub>2</sub>Zr(H)Cl]<sub>n</sub>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 5.76 (s, 10 H, ZrCp), 4.30 (s, 5 H, RuCp), 1.39 (m, 2 H, ZrCH<sub>2</sub>), 1.16 (filled-in doublet, <sup>2</sup>J<sub>PH</sub> + <sup>4</sup>J<sub>PH</sub> = 8.4 Hz, 18 H, PMe<sub>3</sub>), -0.04 (m, 1 H, RuCHD). IR (KBr):  $\nu(\text{agostic CD})$  2031  $\text{cm}^{-1}$ .

**Cp(PMe<sub>3</sub>)<sub>2</sub>RuCD<sub>2</sub>CH<sub>2</sub>ZrClCp<sub>2</sub>, 1-d<sub>2</sub>.** 1-d<sub>2</sub> was prepared from Cp(PMe<sub>3</sub>)<sub>2</sub>RuCD=CH<sub>2</sub> (43 mg, 0.12 mmol) and [Cp<sub>2</sub>Zr(D)Cl]<sub>n</sub> (35 mg, 0.14 mmol) in THF as described for **1**. This gave an orange solid (39 mg, 54% yield, 94% purity, and 98% D). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 5.76 (s, 10 H, ZrCp), 4.30 (s, 5 H, RuCp), 1.39 (br s, 2 H, ZrCH<sub>2</sub>), 1.17 (filled-in doublet, <sup>2</sup>J<sub>PH</sub> + <sup>4</sup>J<sub>PH</sub> = 8.3 Hz, 18 H, PMe<sub>3</sub>). IR (KBr):  $\nu(\text{agostic CD})$  2031  $\text{cm}^{-1}$ .

**Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CHC(O)ZrClCp<sub>2</sub>, 2-CO.** A solution of **2** (331 mg, 0.55 mmol) in THF (10 mL) was charged with CO (1 atm). The solution was stirred overnight, and turned from red-orange to light orange. An aliquot of the solution was checked by <sup>1</sup>H NMR to ensure that the reaction was complete. After filtering through Celite, the THF solution was concentrated, and hexane was added to initiate precipitation. The precipitate was isolated, washed with hexane, and dried under vacuum to give a yellow solid (258 mg, 75% yield, >97% purity by <sup>1</sup>H NMR). Analytically pure crystals were obtained from vapor diffusion of Et<sub>2</sub>O into a concentrated THF solution at room temperature. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 11.70 (dt, <sup>3</sup>J<sub>HH</sub> = 15.8 Hz, <sup>3</sup>J<sub>PH</sub> = 8.6 Hz, 1 H, RuCH), 7.83 (dt, <sup>3</sup>J<sub>HH</sub> = 15.8 Hz, <sup>4</sup>J<sub>PH</sub> = 0.7 Hz, 1 H, RuC=CH), 5.79 (s, 10 H, ZrCp), 4.92 (s, 5 H, RuCp), 1.50 (filled-in doublet, <sup>2</sup>J<sub>PH</sub> + <sup>4</sup>J<sub>PH</sub> = 8.8 Hz, 18 H, PMe<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 0.06 M Cr(acac)<sub>3</sub>): δ 267.5

(s, CO), 246.5 (br d,  $^1J_{\text{CH}} = 131$  Hz, RuCH), 142.5 (d,  $^1J_{\text{CH}} = 151$  Hz, RuC=CH), 108.3 (d,  $^1J_{\text{CH}} = 173$  Hz, ZrCp), 85.1 (d,  $^1J_{\text{CH}} = 175$  Hz, RuCp), 22.7 (q of vt,  $^1J_{\text{CH}} = 122$  Hz,  $^1J_{\text{PC}} + ^3J_{\text{PC}} = 30$  Hz, PMe<sub>3</sub>). IR (KBr):  $\nu(\text{CO})$  1443 cm<sup>-1</sup>, band at 1212 cm<sup>-1</sup> tentatively assigned as  $\nu(\text{C}=\text{C})$  of Zr—C=C (see zwitterionic resonance form). Anal. Calcd for C<sub>24</sub>H<sub>35</sub>ClO<sub>2</sub>RuZr: C, 45.81; H, 5.62. Found: C, 45.61; H, 5.68. Crystals suitable for X-ray diffraction were grown by vapor diffusion of Et<sub>2</sub>O into a THF solution at room temperature.

**Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CMeC(O)ZrClCp<sub>2</sub>.** A solution of Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CMeZrClCp<sub>2</sub> (185 mg, 0.30 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was stirred under CO (1 atm). Aliquots were examined by <sup>1</sup>H NMR to check the extent of reaction. After 10 days, the excess CO and other volatiles were removed under vacuum. The residue was dissolved in THF and worked up as described for 2-CO to give a yellow solid (154 mg, 80% yield, >95% purity by <sup>1</sup>H NMR). Analytically pure crystals were obtained by vapor diffusion of Et<sub>2</sub>O into a concentrated THF solution at room temperature. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  11.32 (t,  $^3J_{\text{PH}} = 11.0$  Hz, 1 H, RuCH), 5.79 (s, 10 H, ZrCp), 4.86 (s, 5 H, RuCp), 2.09 (br s, 3 H, Me), 1.51 (filled-in doublet,  $^2J_{\text{PH}} + ^4J_{\text{PH}} = 8.6$  Hz, 18 H, PMe<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 0.04 M Cr(acac)<sub>3</sub>):  $\delta$  269.3 (s, CO), 242.6 (br d,  $^1J_{\text{CH}} = 135$  Hz, RuCH), 150.1 (s, CMe), 108.7 (d,  $^1J_{\text{CH}} = 173$  Hz, ZrCp), 82.7 (d,  $^1J_{\text{CH}} = 175$  Hz, RuCp), 23.0 (q of vt,  $^1J_{\text{CH}} = 126$  Hz,  $^1J_{\text{PC}} + ^3J_{\text{PC}} = 30$  Hz, PMe<sub>3</sub>), 19.3 (q,  $^1J_{\text{CH}} = 142$  Hz, CMe). IR (KBr):  $\nu(\text{C}=\text{C})$  1446,  $\nu(\text{CO})$  1400 cm<sup>-1</sup>, band at 1209 cm<sup>-1</sup> tentatively assigned as  $\nu(\text{C}=\text{C})$  of Zr—C=C (see zwitterionic resonance form). Anal. Calcd for C<sub>23</sub>H<sub>37</sub>ClO<sub>2</sub>RuZr: C, 46.67; H, 5.81. Found: C, 46.61; H, 5.63.

**Competitive CO Insertion into Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CHZrClCp<sub>2</sub> and Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CMeZrClCp<sub>2</sub>.** In an NMR tube, Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CHZrClCp<sub>2</sub> (~5 mg) in CD<sub>2</sub>Cl<sub>2</sub> was placed under an atmosphere of CO. The reaction was ~70% complete in 30 min as determined by <sup>1</sup>H NMR. In a similar reaction, the reaction of Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CMeZrClCp<sub>2</sub> (10 mg) in CD<sub>2</sub>Cl<sub>2</sub> under CO (1 atm) was ~70% complete in 22 h. A competition experiment directly determined the relative rates at which these two dimetallocenes react with CO. A 5-mm NMR tube was charged with Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CHZrClCp<sub>2</sub> (4.4 mg), Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CMeZrClCp<sub>2</sub> (10.2 mg), 1,4-bis(trimethylsilyl)benzene (internal integration standard), and CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL) to give a Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CMeZrClCp<sub>2</sub>:Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CHZrClCp<sub>2</sub> ratio of 2.78 as determined by <sup>1</sup>H NMR. The CD<sub>2</sub>Cl<sub>2</sub> solution was frozen in liquid N<sub>2</sub>, and CO (1 equiv based on Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CHCZrClCp<sub>2</sub>) was added to the evacuated tube. After 3 days, the relative peak heights of the ZrCp resonances of Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CHC(O)ZrClCp<sub>2</sub>:Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CMeC(O)ZrClCp<sub>2</sub> was 36:1, indicating a kinetic preference of ~102:1 for the insertion of CO into the Zr—C bond of the unsubstituted dimetallocene Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CHZrClCp<sub>2</sub> over the methylated dimetallocene Cp(PMe<sub>3</sub>)<sub>2</sub>RuCH=CMeZrClCp<sub>2</sub>.

**Collection and Reduction of X-ray Data.** In each case, the crystal was coated with petroleum jelly and mounted in a glass capillary. An initial X-ray study was performed at room temperature to determine crystal quality and to identify the crystal system. The crystals were then cooled to 200 K for the collection of intensity data.

**1** crystallizes as yellow-orange prisms. A crystal of dimensions 0.13 × 0.17 × 0.28 mm was used for the X-ray study. (A preliminary report of the structure of this compound has been published.<sup>3</sup>) The diffraction data indicated monoclinic symmetry with systematic absences 0k0, k = 2n + 1, and h0l, h + l = 2n + 1, consistent with the space group P2<sub>1</sub>/n (a nonstandard setting of P2<sub>1</sub>/c).<sup>66a</sup>

**2** crystallizes as yellow prisms. A crystal of dimensions 0.20 × 0.20 × 0.57 mm was used for the X-ray study. The diffraction data indicated orthorhombic symmetry with systematic absences h0l, l = 2n + 1, and hk0, h + k = 2n + 1, consistent with space groups P2<sub>1</sub>cn and Pmcn (a nonstandard setting of Pnma).<sup>66b</sup>

**3** crystallizes as orange-red prisms. A crystal of dimensions 0.40 × 0.40 × 0.10 mm was used for the X-ray study. The diffraction data reflected monoclinic symmetry with systematic absences 0k0, k = 2n + 1, consistent with space groups P2<sub>1</sub> and P2<sub>1</sub>/m.<sup>66c</sup>

**2-CO** crystallizes as orange prisms. A crystal of dimensions 0.20 × 0.22 × 0.40 mm was used for the X-ray study. The diffraction data reflected orthorhombic symmetry with systematic absences 0kl, k + l = 2n + 1, and hk0, k = 2n + 1, consistent with space groups Pn2<sub>1</sub>b and Pnmb (a nonstandard setting of Pnma).<sup>66d</sup>

For **2** and **2-CO**, the solution and refinement of the structures indicated the centrosymmetric space group as the correct choice so the crystal parameters and intensity data were transformed to the standard setting, Pnma, and all data reported here for **2** and **2-CO** refer to the setting Pnma unless otherwise noted.

Crystal data is given in Table I, and additional details of the data collection and reduction are provided in Table S1 (supplementary material).

**Determination and Refinement of the Structures.** **1**, **2**, and **2-CO** were solved by the calculation of a Patterson map<sup>67</sup> to determine the location of the ruthenium atoms followed by a series of difference Fourier maps to locate the remaining non-hydrogen atoms. All the hydrogen atoms for **1**, **2**, and **2-CO** were placed at calculated positions (C—H = 0.95 Å) and allowed<sup>67</sup> to "ride" on the atom to which they were attached, except for the hydrogen atoms on the bridging CH<sub>2</sub>CH<sub>2</sub> group in **1**, which were located on a difference Fourier map before the final cycles of least-squares refinement<sup>67</sup> and fixed at those positions. Hydrogen atoms were not included in the refinement of **3**.

In **2** and **2-CO**, the Ru, Zr, Cl, and the atoms of the bridging ligands are situated on the crystallographic mirror plane. Anisotropic thermal parameters were used for all non-hydrogen atoms except for the cyclopentadienyl ligand on the ruthenium in **2** and **2-CO** and two of the three cyclopentadienyl ligands and two of the three methyl groups on the trimethylphosphine in **3**, which were disordered over two sites. This disordered model was refined with isotropic thermal parameters assuming a 50:50 disordering over the two sites.

The structure of **3** was solved by direct methods in space group P2<sub>1</sub>/m. For this compound, the initial solution and refinement of the structure, with the Ru, Zr, C(1), and C(2) situated on the crystallographic mirror plane and the other ligands disordered by the crystallographic mirror plane, resulted in unsatisfactory thermal ellipsoids and bond distances. Several models were tried to improve the structure, and the one that gave the best results is reported here, with the Ru atom disordered about the crystallographic mirror plane. The Zr atom, C(1), and C(2) are so close to the mirror plane that they had to be fixed on the mirror during refinement. The increase in the Zr—Cl bond length of 2.652 (6) Å observed in **3** (compared to Zr—Cl distances of 2.583 (5) Å in **2** and 2.579 (3) Å in **1**) is probably a result of fixing the Zr to the mirror plane, and is not considered to be significant.

A common isotropic thermal parameter was refined for all the hydrogen atoms for **1**, **2**, and **2-CO**. ( $U = 0.063$  (7) Å<sup>2</sup> for **1**,  $U = 0.12$  (2) Å<sup>2</sup> for **2**, and  $U = 0.08$  (1) Å<sup>2</sup> for **2-CO**.) The quantity  $\sum w(|F_o| - |F_c|)^2$  was minimized during the least-squares refinement using absorption corrected data and neutral atom scattering factors<sup>66d</sup> and corrections for anomalous dispersion effects.<sup>66d</sup> For **3**, the data were also scaled<sup>68</sup> to correct for a decay (~15%, see supplementary material) of the crystal during data collection. Selected interatomic distances and angles are listed in Table II.

Additional crystallographic information is provided in Tables S1–S20 (supplementary material).

**Acknowledgment.** This research was carried out at Brookhaven National Laboratory under Contract DE-AC02-76CH0016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. We thank Drs. Mark Andrews and George Gould for helpful suggestions and discussions. We thank Profs. Wolfgang Beck and John P. Selegue for preprints of related work and helpful comments and Prof. Michael E. Wright for suggesting the preparation of Cp(PMe<sub>3</sub>)<sub>2</sub>RuC≡CSnMe<sub>3</sub>.

**Supplementary Material Available:** Tables of experimental details of the X-ray diffraction structures of **1**, **2**, **3**, and **2-CO**, final non-hydrogen atomic positional parameters (Tables S6, S9, S13, and S17), final thermal parameters for the non-hydrogen atoms (Tables S7, S10, S14 and S18), hydrogen atom positions (Table S11, S15 and S19), and complete listing of interatomic distances and angles (Table S2–S5) (27 pages); a listing of observed and calculated structure factors (Tables S8, S12, S16, and S20) (35 pages). Ordering information is given on any current masthead page.

(66) *International Tables for X-Ray Crystallography*, 3rd ed.; Kynoch Press: Birmingham, England, 1969; (a) Vol. 1, p 99; (b) Vol. 1, p 151; (c) Vol. 1, p 93; (d) Vol. IV, pp 99–101 and 149–150.

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