# Cationic Ruthenium Hydrido-Carbonyls Derived from Metallocene-Based Pincers: Unusual Rearrangements and H<sub>2</sub> Evolution with Formation of Cationic Ruthenium Metallocenylidenes

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Cationic ruthenium hydrido-carbonyls {RuH(CO)[ $^{\prime Bu}$ P,CH,P<sup>M</sup>]}BAr<sup>F</sup><sub>4</sub> (M = Fe, **3**; M = Ru, **4**) (Ar<sup>F</sup> = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) obtained in the reaction of H<sub>2</sub> with RuCl(CO)[ $^{\prime Bu}$ P,C,P<sup>M</sup>](M = Fe, **1**; M = Ru, **2**) in the presence of NaBAr<sup>F</sup><sub>4</sub> add CO smoothly, giving the corresponding dicarbonyl complexes {RuH(CO)<sub>2</sub>[ $^{\prime Bu}$ P,CH,P<sup>M</sup>]}BAr<sup>F</sup><sub>4</sub> (M = Fe, **11**; M = Ru, **12**). According to X-ray analysis of **11** and **12**, addition of extra CO to complexes **3** and **4** leads to strengthening of the C(1)-H(1)···Ru(1) agostic interaction. Simultaneously, CO addition to **3** and **4** triggers a sequence (up to three steps) of unprecedented intramolecular rearrangements including migration of H atoms. First metallocenylidene complexes {Ru(CO)<sub>2</sub>[ $^{\prime Bu}$ P,C,P<sup>M</sup>]}BAr<sup>F</sup><sub>4</sub> (M = Fe, **15**; M = Ru, **16**) were obtained in the course of these rearrangements accompanied by H<sub>2</sub> evolution.

#### Introduction

Formation and cleavage of dihydrogen on transition metal complexes has attracted much attention in recent years because of their application in hydrogenation and relevance to hydrogen production.<sup>1</sup> The dihydrogen activation may occur via two different mechanisms, homolytic and heterolytic, and the latter is of great importance in biological systems<sup>1d</sup> and catalytic ionic hydrogenations.<sup>1e,f</sup> One of the remarkable properties of transition metal hydride complexes formed is the ability to undergo intramolecular rearrangements; well-known examples of hydrogen migration are fluxionality of hydride ligands in transition metal clusters.<sup>2</sup> Even more interesting in view of chemical reactivity is

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intramolecular exchange of the hydrogen atoms between transition metal and carbon (nitrogen) atoms<sup>3</sup> in connection with processes such as hydrogenation, isomerization, dehydrogenation, and other chemical transformations of organics.

ORGANOMETALLICS

Herein we describe an unusual set of intramolecular rearrangements that we observed in the course of the study of reactions of  $H_2$  with cationic ruthenium carbonyl pincer complexes based on ferrocene and ruthenocene. After addition of  $H_2$  to these complexes, coordination of an extra CO ligand to the ruthenium atom promotes a sequence (up to three steps) of intramolecular rearrangements, leading to  $H_2$  evolution and formation of the first (cationic) metallocenylidene complexes.

## **Results and Discussion**

Formation of Complexes {RuH(CO)[{2,5-( ${}^{7}Bu_2PCH_2$ ) $_2C_5H_3$ }-M(C<sub>5</sub>H<sub>5</sub>)]}BAr<sup>F</sup><sub>4</sub> (M = Fe, 3; M = Ru, 4). Complexes 3 and 4 were obtained quantitatively in clean reactions of the corresponding chloro-carbonyl ruthenium complexes RuCl(CO)[{2,5-( ${}^{7}Bu_2PCH_2$ )} $_2C_5H_2$ }M(C<sub>5</sub>H<sub>5</sub>)] (M = Fe, 1; M = Ru, 2) with H<sub>2</sub> in the presence of NaBAr<sup>F</sup><sub>4</sub> (Ar<sup>F</sup> = 3,5-(CF<sub>3</sub>)} $_2C_6H_3$ ) (eq 1).



Complex 3 was characterized by a single-crystal X-ray diffraction. The molecular structure of 3 is illustrated in



Figure 1. Molecular structure of 3 (ellipsoids at the 50% probability level; hydrogen atoms except H(1M) and H(1) and BAr<sup>F</sup><sub>4</sub> anion are omitted for clarity). Selected bond lengths [Å] and angles [deg]: Ru(1)-P(1) 2.3847(6), Ru(1)-P(2) 2.3856(6), Ru(1)-C(1) 2.326(2), Ru(1)-C(29) 1.809(3), Ru(1)-H(1M) 1.64, Fe(1)-C(1) 2.035(2), Fe(1)-C(2-10) 2.023(2)-2.065(3), C(1)-C(2) 1.447(3), C(1)-C(5) 1.458(3), C(1)-H(1) 0.91, C(2)-C(3) 1.424(4), C(3)-C(4) 1.431(4), C(4)-C(5) 1.417(3), P(1)-Ru(1)-P(2) 166.92(2), C(29)-Ru(1)-C(1) 171.1(1), C(2)-C(1)-C(5) 108.0(2), C(2)-C(1)-Ru(1) 97.4(1), C(5)-C(1)-Ru(1) 96.5(2), Ru(1)-C(1)-H(1) 96.

Figure 1. As is seen, the structure is unusual for a ferrocene derivative. The complex bears two substituents on the C(1)atom of the cyclopentadienyl ring: the hydrogen H(1) and the ruthenium Ru(1) atoms arranged in the endo and exo positions, respectively, relative to the metallocene central atom Fe(1). The C(1)–H(1) bond forms an angle of  $16.5^{\circ}$  with the ring plane, and the Ru(1)-C(1) vector forms an angle of 79.1° with the same plane. The second hydrogen atom from the reacting  $H_2$  molecule occupies the apical position at the pentacoordinated Ru(1) atom; the H(1M) and H(1) hydrogen atoms are in the *transoid* orientation along the Ru(1)-C(1) bond. Thus, the Ru(1) atom has a distorted tetragonal pyramid configuration; Ru(1), P(1), P(2), and C(29) atoms lie in the basal plane (maximum deviation of 0.014 Å for Ru(1)), whereas the C(1) atom deviates from this plane by 0.40 Å in the opposite direction from the H(1M) atom, and the Ru(1)-H(1M) bond forms an angle of 85.2° with this plane. The structure of complex 3 does not reveal any agostic  $Ru(1) \cdots H-C$  interaction with the participation of C-H sp<sup>3</sup> bonds of the tert-butyls, as well as close contacts with the  $BAr_{4}^{F_{4}}$  counterion.

In complex **3**, the substituted carbocyclic ligand is almost planar; the C(1) atom deviates from the plane of the other carbon atoms toward the Ru(1) atom only by 0.02 Å. The C(1)-C(2) and C(1)-C(5) distances (1.447(3) and 1.458(3) Å, respectively) are somewhat longer (by about 0.03 Å) than the C(2)-C(3) and C(4)-C(5) distances (1.424(3) and 1.417(3) Å, respectively), whereas the C(3)-C(4) bond has an intermediate length (1.431(4) Å). The differences in C-C bond lengths in the five-membered carbocycle can be considered as evidence for the contribution of the ferrocenium ion structure. (Here the term "ferrocenium" means cationic species related to the arenium ions, in contrast to cationic species oxidized at the iron atom, for which the term "ferricenium" seems to be more appropriate.) Noteworthy, the hydrogen atom H(1) is almost equally remote from both metal atoms: the H(1)...Fe(1) and H(1)...Ru(1) distances are 2.50 and 2.58 Å, respectively. These distances are too large to suppose marked (if any) interaction between the hydrogen atom H(1) and any of the above metal atoms, though it is reported that the distances for intramolecular M...HC bonds can vary in a wide range,<sup>4a</sup> from 1.84 Å for a manganese complex<sup>4b</sup> to 2.92 Å for a palladium complex.<sup>4c</sup>

Spectroscopic data obtained for **3** in solution are in accordance with its solid-state X-ray crystal structure. In the <sup>1</sup>H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>), there are resonances from the H(1) atom at  $\delta$  2.03 ppm (s) and the hydride atom at  $\delta$  –26.22 ppm (t,  $J_{(H-P)}$ =15.9 Hz). Such a high-field hydride resonance is typical of a hydride ligand *trans* to a vacant coordination site. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, a resonance from the C(1) carbon is observed at  $\delta$  37.92 ppm (s). Spectral characteristics for the diruthenium complex **4** are similar to those for complex **3**.

The DFT calculations for complexes 3 and 4 gave geometrical parameters close to those obtained by the X-ray diffraction method for complex 3 (see Table 1 in the SI), thus confirming that the above peculiarities of the structure are associated with the molecular properties rather than with crystal-packing forces.

The IR spectrum of complex **3** in solution contains a strong band at 1943 cm<sup>-1</sup> belonging to  $\nu$ (CO) and a very weak band at 2020 cm<sup>-1</sup> belonging to  $\nu$ (Ru-H) (see Figure 1 in the SI). The intensity ratio is in accordance with the DFT data, which show that the former band is 40-fold more intense than the latter. It should be noted that the calculated  $\nu$ (CO) frequency matches very well the experimental frequency, but the calculated  $\nu$ (MH) is higher due to anharmonicity.

Consideration of the structure of complex 3 does not provide information on the mechanism of its formation; it is evident, however, from the *transoid* arrangement of C(1)-H and Ru(1)-H hydrogen atoms along the C(1)-Ru(1) bond that after H<sub>2</sub> addition some rearrangement(s) take place, giving finally complex 3. At present, a mechanistic pathway can be proposed involving H<sub>2</sub> activation/hydrogenolysis of the C(1)-Ru(1) bond followed by *exo* attack of the cyclopentadienyl C(1)-H(1) carbon atom with the cationic (chelated) ruthenium hydrido-carbonyl fragment.

As for formation of complexes **3** and **4**, it is interesting that they can also be generated by protonation of carbonyl hydrides  $\text{RuH}(\text{CO})[\{2,5-(^{t}\text{Bu}_2\text{PCH}_2)_2\text{C}_5\text{H}_2\}\text{M}(\text{C}_5\text{H}_5)]$ , **5** (M = Fe) and **6** (M = Ru), respectively. The latter can be obtained from **3** and **4**, respectively, by the abstraction of the H(1) atom as a proton under the action of amines (NEt<sub>3</sub> or Py); however, several unidentified complexes are simultaneously formed in these reactions. Pure complex **5**, containing the hydride ligand in the *exo* position, was isolated in the reaction of complex **1** with LiAlH<sub>4</sub> (eq 2). Its protonation with CF<sub>3</sub>COOH gave the cationic complex **3**\* (eq 3). Chemical shifts of the C(1)-*H* and Ru(1)-*H* hydrogen atoms for complex **3**\* are practically the same as those observed for

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Figure 2. Benzene-based cationic pincer complexes.

complex 3, indicating the absence of hydrogen bonding with the anion  $CF_3CO_2^{-1}$ .



It should be noted that several cationic organometallic complexes with structures similar to those of **3** and **4** generated from benzene-based pincer complexes are described in the literature<sup>5-8</sup> (see Figure 2). While platinum  $7^5$  and ruthenium  $8^6$  complexes are considered essentially as transitionmetal-stabilized arenium ions (mainly on the basis of X-ray diffraction data), rhodium  $9a,b^7$  and ruthenium  $10^8$  complexes are thought to be "agostic", containing the C(1)–H(1)···M bond with an insignificant contribution of the arenium structure (for example, in complex 9a the C(1)-H···Rh distance is only 1.950 Å).

Formation of Complexes { $RuH(CO)_2[{2,5-('Bu_2PCH_2)_2-C_5H_3}M(C_5H_5)]$ }BAr<sup>F</sup><sub>4</sub> (M = Fe, 11; M = Ru, 12) and Their Rearrangements. Ruthenium complexes 3 and 4 are coordinatively unsaturated 16-electron compounds and add readily CO to form dicarbonyl derivatives 11 and 12, respectively (Scheme 1). They were fully characterized by spectroscopic

methods and single-crystal X-ray diffraction (see Figures 3 and 4). As expected, the incoming CO occupies a vacant coordination position at the chelated ruthenium atom in complexes 3 and 4. On the whole, the structures of complexes 11 and 12 are similar to those of their precursors 3 and 4.

The most remarkable are the distances between the hydrogen atom H(1) and the chelated Ru(1) and metallocene central atoms in complexes **11** and **12**. In complex **11**, they are 2.36 and 2.49 Å, respectively; that is, on going from monocarbonyl to dicarbonyl complex, the H(1) $\cdots$ Fe(1) distance does not virtually change, whereas the H(1) $\cdots$ Ru(1) distance is somewhat decreased (compare 2.58 and 2.36 Å). A close value of the H(1) $\cdots$ Ru(1) distance (2.39 Å) is observed for complex **12** with the ruthenocene backbone, whereas the distance between the same hydrogen and the ruthenocene central atom, Ru(2), is 2.57 Å. Although these changes in the distances are relatively small, the trends in their changes can indicate the existence of a C(1)– H(1) $\cdots$ Ru(1) agostic interaction. This interaction is weak, as follows from the large distances H(1) $\cdots$ Ru(1).

In addition, we note that the C(1)-H(1) bond forms an angle of 17.3° and 19.6° (for 11 and 12, respectively) with the ring plane, and the Ru(1)-C(1) vector forms an angle of 64.1° (11) and 63.1° (12) with the same plane. In comparison to complex 3, vector C(1)-H(1) does not change its direction relative to the five-membered ring, whereas vector C(1)-Ru(1) markedly deviates from perpendicular to this plane. It can also indicate some agostic  $C(1)-H(1)\cdots$ Ru(1) interaction. The DFT-calculated structures of complexes 11 and 12 are similar and close to those obtained by X-ray diffraction.

IR spectra of dicarbonyl complexes 11 and 12 look quite exceptional. Usually the bands of M-H stretching vibration are very weak; therefore, two intense bands of  $\nu(CO)$  and one weak band of  $\nu$ (MH) are expected in the range of 2000 cm<sup>-</sup> However, absorptions at 2057, 2001, and 1958 cm<sup>-1</sup> of approximately equal intensities (intensity ratio is 1:1.16:0.81) are observed for complex 11 (Figure 1 in the SI); the bands at 2001 and 1958 cm<sup>-1</sup> mainly belong to symmetrical and asymmetrical  $\nu$ (CO) stretching, and the band at 2057 cm<sup>-1</sup> is mainly associated with the Ru–H mode. The unusually high intensity of the  $\nu(MH)$  band results from strong coupling of C-O and Ru-H stretching vibrations due to the mutual trans arrangement of the CO and H ligands, which leads to the redistribution of band intensities. The DFT calculation predicts for complex 11 three intense bands at 2020, 1975, and 1924  $\text{cm}^{-1}$  with the intensity ratio of 1:1:0.66.

Two extreme canonical forms, metallocenium ion (A) and cationic agostic complex (B), can be considered for complexes 11 and 12 (Scheme 2). Alternation of C–C distances in the five-membered ring of complexes 11 and 12 (see Figures 3 and 4 for structural parameters), similar to those observed for complexes 3 and 16 (see Scheme 1), implies that structure A has a substantial contribution. Nevertheless, although the C(1)H(1)···Ru(1) distances (2.58, 2.36, and 2.39 Å) and H(1)–C(1)–Ru(1) angles (96°, 82°, and 83°) for complexes 3, 11, and 12, respectively, do not allow us to delineate "agostic" or anagostic<sup>\*10</sup> interactions, they suggest that in these complexes some C(1)–H(1)···Ru(1) interaction takes place.

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Scheme 1. Reactions of 3 and 4 with CO Result in Hydrido Dicarbonyls 11 and 12<sup>a</sup>



<sup>*a*</sup> Further isomerization of the latter complexes into 13 and 14 and subsequent expulsion of  $H_2$  afford metallocenylidene complexes 15 and 16 and agostic complex 17.<sup>9</sup>

In CD<sub>2</sub>Cl<sub>2</sub> solution, complex **11** slowly rearranges into isomer **13**, where the hydrogen atoms C(1)-*H* and Ru(1)-*H* are *cis* arranged along the C(1)–Ru(1) line (Scheme 1). The conclusion on the structure of **13** is drawn from spectroscopic data. Thus, in the <sup>1</sup>H NMR spectrum of complex **13**, the hydride signal at  $\delta$  –5.08 (dt) undergoes splitting with  $J(_{H-H}) \approx 1.0$  and  $J(_{P-H}) = 15.5$  Hz, while in the case of its precursor, **11**, the signal at  $\delta$  –6.08 (dt) is split with  $J(_{H-H}) =$ 2.7 and  $J(_{P-H}) = 15.5$  Hz. The lower value of  $J(_{H-H})$  for **13** indicates mutual *cisoid* arrangement of the hydrogen atoms C(1)-*H* and Ru(1)-*H* in this complex. (In contrast to **13**, its diruthenium analogue, **14**, appears unstable under the same conditions and was not fully characterized.)

The rearrangement might include the rupture of the relatively weak C(1)-Ru(1) bond (2.315(2) and 2.326(3) Å for **11** and **12**, respectively), accompanied by migration of the Ru(1)-*H* hydrogen atom to the C(1) carbon and the C(1)-*H* hydrogen atom to the Ru(1), and subsequent *exo* electrophilic attack of ruthenium at the ring. The C(1)-Ru(1)-H(1M) and H(1)-C(1)-Ru(1) angle values for **11** (87° and 82°, respectively) and **12** (78° and 83°, respectively) can be considered as possible indications that such migration of H(1) and H(1M) atoms includes the rearrangement of the *transoid* complexes **11** and **12** into the corresponding *cisoid* isomers. For monocarbonyl complex **3**, the C(1)-Ru(1)-H(1M) and H(1)-C(1)-Ru(1) angles are 99° and 96°, respectively.

Milstein et al. have reported<sup>11</sup> the formation of benzenebased ruthenium pincer complex {RuH(CO)<sub>2</sub>[2,6-(<sup>7</sup>Bu<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>]}<sup>+</sup>, with a structure similar to that of complex **13**. This complex, unstable at room temperature, was obtained by reversible addition of H<sub>2</sub> to cationic dicarbonyl complex {Ru(CO)<sub>2</sub>[2,6-(<sup>7</sup>Bu<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]}<sup>+</sup>. Although the complex was not studied by X-ray diffraction, it is thought to contain the agostic C(1)-H···Ru bond. In contrast to {Ru(CO)<sub>2</sub>-[2,6-(<sup>7</sup>Bu<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]}<sup>+</sup>, the metallocene-derived dicarbonyl complex **17** as well as **15** and **16** (see Scheme 1) do not react with H<sub>2</sub> under the same conditions (1 atm H<sub>2</sub>, 25 °C).

After isomerization of complexes 11 and 12 into complexes 13 and 14, respectively, the latter, while being kept in  $CD_2Cl_2$  solutions, release dihydrogen to form dicarbonyl complexes 15 and 16, respectively (Scheme 1). (It should be noted that reaction of 1 and 2 with CO in the presence of NaBAr<sup>F</sup><sub>4</sub> afforded complexes 17<sup>9</sup> and 16, respectively.) Apparently, the mutual *cisoid* orientation of two hydrogen atoms in complexes 13 and 14 favors H<sub>2</sub> elimination. In addition, attractive interaction of acidic C(1)-*H* and hydridic Ru(1)-*H* hydrogens can also lower the barrier for elimination.

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Figure 3. Molecular structure of 11 (ellipsoids at 30% probability level; hydrogen atoms except H(1M) and H(1) and BAr<sup>F</sup><sub>4</sub> anion are omitted for clarity). Selected bond lengths [Å] and angles [deg]: Ru(1)–P(1) 2.4152(7), Ru(1)–P(2) 2.449(8), Ru(1)–C(1) 2.315(2), Ru(1)–C(29) 1.847(3), Ru(1)–C(30) 1.970(3), Ru(1)–H(1M) 1.68, Fe(1)–C(1) 2.050(2), Fe(1)–C(2–10) 2.023-(3)–2.074(3), C(1)–C(2) 1.454(4), C(1)–C(5) 1.453(3), C(1)–H(1) 0.90, C(2)–C(3) 1.423(4), C(3)–C(4) 1.425(4), C(4)–C(5) 1.423(3), P(1)–Ru(1)–P(2) 156.2(2), C(29)–Ru(1)–C(1) 172.8(1), C(30)–Ru(1)–H(1M) 175, C(2)–C(1)–C(5) 107.7(2), C(2)–C(1)–Ru(1) 104.8(2), C(5)–C(1)–Ru(1) 106.7(2), Ru(1)–C(1)–H(1) 82.

The structure of complex **16** was established by X-ray diffraction study (Figure 5).

It is apparent at first glance that the structure of complex 16 resembles those of  $\alpha$ -metallocenyl carbocations.<sup>12</sup> It is known that when the latter are formed from metallocene derivatives (upon reactions of  $\alpha$ -metallocenylethylenes or  $\alpha$ -metallocenylcarbinols with acids), the substituted cyclopentadienyl ligand transforms into pentafulvene; the latter is bound to the metal atom via the six carbon atoms (the strength of the  $M-C_{\alpha}$  bond depends on the electronic and steric properties of the substituents at the  $C_{\alpha}$  atom; the same factors determine the bend of the exocyclic bond  $C(1)-C_{\alpha}$ toward M in the given metallocenyl carbocation). Similar to  $\alpha$ -metallocenyl carbocations, in 16 the exocyclic C(1)-Ru(1) bond is bent toward the metallocene central atom Ru(2) by 29.5°. For comparison, the bending angle of the exocyclic bond out of the C<sub>5</sub> ring in the  $\alpha$ -ruthenocenyl carbocation<sup>12c</sup>  $[RcCH_2][CF_3SO_3]$  (Rc = ruthenocenyl) is 42.6°. Similar strong bending of the exocyclic bond was found for transition metal fulvene compexes.<sup>13</sup> In complex 16, fivemembered carbocycles are nonparallel: the angle between the rings is 19.2°. This strong deviation from parallel, in comparison with  $\alpha$ -metallocenyl carbocations<sup>12</sup> (for complex  $[RcCH_2][CF_3SO_3]$  the ring tilt is only 7.1°), is apparently associated with steric contacts between the pseudoequatorial



Figure 4. Molecular structure of 12 (ellipsoids at 30% probability level; hydrogen atoms except H(1M) and H(1) and BAr<sup>F</sup><sub>4</sub> anion are omitted for clarity). Selected bond lengths [Å] and angles [deg]: Ru(1)-P(1) 2.419(1), Ru(1)-P(2) 2.414(1), Ru(1)-C(1) 2.326(3), Ru(1)-C(29) 1.844(4), Ru(1)-C(30) 1.972(4), Ru(1)-H(1M) 1.70, Ru(2)-C(1) 2.181(3), Ru(2)-C(2-10) 2.153(3)-2.209(3), C(1)-C(2) 1.444(5), C(1)-C(5) 1.453(5), C(1)-H(1) 0.93, C(2)-C(3) 1.419(5), C(3)-C(4) 1.429(5), C(4)-C(5) 1.420(5), P(1)-Ru(1)-P(2) 155.95(3), C(29)-Ru(1)-C(1) 170.6(2), C(30)-Ru(1)-H(1M) 176, C(2)-C(1)-C(5) 108.1(3), C(2)-C(1)-Ru(1) 105.0(2), C(5)-C(1)-Ru(1) 106.7(2), Ru-(1)-C(1)-H(1) 83.

## Scheme 2. Description of Complexes 11 and 12 as Two Extreme Forms, Ferrocenium A and Agostic B



*tert*-butyl groups and the nonmetalated cyclopentadienyl ring: the effect of these contacts on the ring tilt in metallocene-derived pincer complexes of palladium was unambiguously demonstrated earlier.<sup>14</sup> Thus, a comparative X-ray diffraction study of complexes PdCl[{2,5-('Bu<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>- $C_5H_2$ }Ru(Cp')] (Cp' =  $C_5H_5$ , **18**; Cp' =  $C_5Me_5$ , **19**) showed that deviations of the cyclopentadienyl rings in complexes **18** and **19** from parallel are 2.6° and 10.1°, respectively.<sup>14b</sup>

We suggest that unless there is steric contact between the pseudoequatorial *tert*-butyl groups and the nonmetalated cyclopentadienyl ring, stronger bending of the exocyclic bond and a shorter Ru(1)-Ru(2) distance should be expected. The consequence of the above-mentioned steric contacts in **16** is the hindrance to the approach of the Ru(1) atom to Ru(2); this may be the reason for the long Ru(1)-Ru(2) distance

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Figure 5. Molecular structure of one of the two crystallographically independent molecules of 16 (ellipsoids at 30% probability level; hydrogen atoms and BAr<sup>F</sup><sub>4</sub> anion are omitted for clarity). Selected bond lengths [Å] and angles [deg]: Ru(1)–Ru(2) 3.1092(5), Ru(1)–P(1) 2.434(1), Ru(1)–P(2) 2.442(1), Ru(1)–C(1) 2.009(4), Ru(1)–C(29) 1.862(4), Ru(1)–C(30) 1.893(5), Ru(2)–C(1) 2.194(4), Ru(2)–C(2–10) 2.161(4)–2.237(5), C(1)–C(2) 1.454(6), C(1)–C(5) 1.451(5), C(2)–C(3) 1.419(6), C(3)–C(4) 1.444(6), C(4)–C(5) 1.422(6), P(1)–Ru(1)–P(2) 152.34(4), C(29)–Ru(1)–Ru(2) 174.0(1), C(30)–Ru(1)–C(1) 143.4(2), C(29)–Ru(1)–C(1) 129.4(2), C(29)–Ru(1)–C(30) 87.2(2), C(30)–Ru(1)–Ru(2) 98.8(2), C(1)–Ru(1)–Ru(2) 44.6(1).

(3.1092(5) A) in comparison with Ru–Ru bond distances, which generally range from 2.65 to 2.90 Å. However there are precedents for similar long Ru–Ru distances in ruthenium complexes.<sup>15</sup> The Ru–Ru distance of 3.141(2) Å is longer than the normal Ru–Ru bond length in diruthenium carbonyl complexes,<sup>15a</sup> but it is still within the range of bonding distances.<sup>15b</sup> In any case, strong bending of the exocyclic C(1)–Ru(1) bond toward the Ru(2) atom might be explained as a result of *bonding interaction of the Ru*(2) *atom with the exocyclic substituent*.

It does not seem possible to describe unambiguously the Ru(1) polyhedron in complex 16. If this atom is assumed as pentacoordinative (neglecting the Ru(1)-Ru(2) interaction), its coordination sphere can be considered as strongly distorted trigonal bipyramidal with the phosphorus atoms in the apical positions (P(1)-Ru(1)-P(2)) angle is  $152.34(4)^{\circ}$ ; C(1), C(29), and C(30) atoms lie in the equatorial plane; Ru(1) lies in this plane with an accuracy of 0.004 A). However the  $C(30) - Ru(1) - C(1) (143.4(2)^{\circ}), C(29) - C(1) - C(1) (143.4(2)^{\circ}), C(29) - C(1) -$ C(1) (129.4(2)°), and C(29)-Ru(1)-C(30) (87.2(2)°) angles differ very strongly from the ideal value of 120° for a trigonal bipyramid. Taking into account the Ru(1)-Ru(2) interaction, the Ru(1) atom has a coordinative number equal to 6; however, the polyhedron is strongly distorted from the octahedral geometry (see angle values in the caption to Figure 5).

Scheme 3. Description of Complexes 15 and 16 as Two Canonical Forms, C and D



As in the case of  $\alpha$ -metallocenyl carbocations, two extreme canonical forms can be considered for bonding of substituted ligands in cationic complexes **15** and **16** (Scheme 3). The structure **C** is similar to that of cationic  $\eta^5$ -cyclopentadienyl- $\eta^6$ -fulvene-metal(II) complexes, whereas structure **D** resembles bonding of a fulvene ligand in early transition metal complexes, <sup>16</sup> where the  $\eta^6$ -ligand has little fulvene character and the metalated  $\eta^5, \eta^1$ -bonding description is more preferable; in this case the formal oxidation state of the metallocene central atom should be M(IV).

Another remarkable feature of the structure of complex 16 is that alternation of the carbon-carbon distances in the substituted ligand is very similar to that observed for the  $\alpha$ -ruthenocenyl carbocation [RcCH<sub>2</sub>][CF<sub>3</sub>SO<sub>3</sub>].<sup>12c</sup> Thus, for 16 (crystallographic isomer A) the C–C distances are C(1)– C(2) 1.454(6), C(1)-C(5) 1.451(5), C(2)-C(3) 1.419(6), C(4)-C(5) 1.422(6), and C(3)-C(4) 1.444(6) Å, whereas for [RcCH<sub>2</sub>][CF<sub>3</sub>SO<sub>3</sub>], the corresponding distances are 1.458(6), 1.459(6), 1.413(7), 1.412(6), and 1.429 Å, respectively. In the case of the ruthenocenyl carbocation, the alternation of the C-C bond lengths was considered as consistent with the description of the C<sub>5</sub>H<sub>4</sub>CH<sub>2</sub> ligand as a coordinated fulvene similar to some substituted ( $\eta^6$ -fulvene)- $Cr(CO)_6$  derivatives<sup>13c</sup>. On the other hand, for structure **D**, we may expect equalization of bond lengths in the  $\eta$ -cyclopentadienyl ring and lengthening of the exocyclic bond. It should be noted that the C(1)-Ru(1) distance (2.009(4) Å) in complex 16 is shorter than the ordinary C(1)-Ru(1) bond in ruthenium pincer complexes with the metallocene backbone; for example, in isomeric cationic complex  $17^9$  (see Scheme 1) it is equal to 2.047(3) Å.

Altogether, the comparison of the X-ray diffraction data for **16** with the structural data for the known  $\alpha$ -metallocenyl carbocation and fulvene complexes gives reason to consider complex **16** as essentially a cationic ruthenium ruthenocenylidene. The formation of pincer complexes with the carbene backbone was reported in the literature;<sup>17</sup> however, to the best of our knowledge, metallocenylidene complexes have not been obtained.

Complex 15 is less stable than 16; in solution it rearranges into the known agostic complex  $17^9$  (Scheme 1). Apparently, in 15 the metallocene central atom is bound to the chelated ruthenium atom weaker than in 16, which explains the higher inclination of complex 15 to this rearrangement as compared

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to that of its diruthenium analogue **16**. Earlier complex [Fc\*CHRc]BF<sub>4</sub> (Fc\* is ferrocenyl-<sup>57</sup>Fe) was studied by <sup>13</sup>C and <sup>57</sup>Fe NMR, and it was found that the iron atom cannot compete with the ruthenium atom for binding with the "carbocationic center"  $C_{\alpha}$ ; as a result, the positive charge is delocalized on the Rc fragment.<sup>18</sup>

DFT calculations for complexes 15 and 16 are also in agreement with the X-ray data (see Table 2 in the SI). The Ru(1) atom deviates from the ring plane toward the Fe (or Ru) atoms of the metallocene backbone. The calculation predicts two  $\nu$ (CO) bands in the IR spectra of approximately equal intensities, which is in accord with the experimental values. The DFT calculations revealed that complex 15, where the Ru(1) atom deviates from the ring plane toward the Fe(1) atom by 28.9°, is 3.9 kcal/mol less favorable than agostic complex 17, where the Ru(1) atom deviates to the opposite side by 9.3°, which is in accordance with X-ray data (10.5°). This difference is small, but it can be the driving force of the rearrangement of 15 into 17.

## **Concluding Remarks**

Novel cationic ruthenium complexes were obtained by the reaction of ruthenium chloro-carbonyl metallocene-based pincer complexes with H<sub>2</sub> in the presence of NaBAr<sup>F</sup><sub>4</sub>. Additionally, it was demonstrated that the same complexes can be obtained by the protonation of the appropriate ruthenium hydrido-carbonyls. The structures of cationic ruthenium hydrido-carbonyls and the ways of their formation are interesting in light of the mechanism of electrophilic substitution/ protonation in iron group metallocenes.<sup>19</sup> After CO addition, these complexes undergo a sequence (up to three steps) of unprecedented intramolecular rearrangements. First metallocenylidene complexes were obtained in the course of these rearrangements accompanied by dihydrogen evolution. The mechanism of formation of complexes 3 and 4 and reactivity of cationic ruthenium hydrido-carbonyls and metallocenylidene complexes are currently under study.

## **Experimental Section**

**General Considerations.** All reactions were carried out under a purified argon atmosphere. All solvents were refluxed and distilled over appropriate reagents under an argon atmosphere. Deuterated solvents were degassed with argon. The NMR spectra were recorded on Bruker Avance 300, 400, and 600 MHz spectrometers. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR chemical shifts are reported in parts per million downfield from tetramethylsilane; for <sup>1</sup>H NMR spectra residual signals of deuterated solvents were used as references (7.26 ppm for CDCl<sub>3</sub>, 7.16 ppm for C<sub>6</sub>D<sub>6</sub>, 5.32 ppm for CD<sub>2</sub>Cl<sub>2</sub>) (s, singlet; br s, broad singlet; d, doublet; t, triplet; vt, virtual triplet). In <sup>13</sup>C{<sup>1</sup>H} NMR measurements the signals of CD<sub>2</sub>Cl<sub>2</sub> (53.7 ppm) or CDCl<sub>3</sub> (77.0 ppm) were used as references. <sup>31</sup>P{<sup>1</sup>H} NMR chemical shifts are reported in parts per million downfield from H<sub>3</sub>PO<sub>4</sub> and referenced to an external

85% solution of phosphoric acid in D<sub>2</sub>O. Complete signal assignments were made using COSY, NOESY, HMQC, and HMBC spectra (see Supporting Information). IR spectra were recorded on a Magna 750 IR (Nicolet) FTIR spectrometer with a resolution of 2 cm<sup>-1</sup>. Calculations were performed using the PRIRODA program<sup>20</sup> and PBE functional<sup>21</sup> with 3z (includes functions for elements up to Xe) and sbk (includes functions for elements heavier than Xe up to radon) basis sets. Results obtained with these basis sets are practically the same. No scaling for calculated IR frequencies was applied. Elemental analyses were performed at the A.N. Nesmeyanov Institute of Organoelement Compounds of RAS. Satisfactory elemental analysis for complexes 4 and 5 could not be obtained due to their instability. The products, however, appear to be analytically pure, as indicated by NMR. The synthesis and spectral and structural data for complexes 1 and 17 were reported earlier.<sup>9</sup> Their diruthenium counterpart, 2, was synthesized by a similar procedure. NaBAr<sup>F</sup><sub>4</sub> was purchased from Aldrich.

Synthesis of  $\text{RuCl}(\text{CO})[f^{\text{Bu}}\text{P},\text{C},\text{P}^{\text{Ru}}]$  (2).  $\text{RuCl}_2(\text{DMSO})_4$  (560 mg, 1.156 mmol) and  $\text{NEt}_3$  (230 mg, 2.277 mmol) were added to a solution of  $\{1,3-(CH_2P'Bu_2)_2C_5H_3\}Ru(C_5H_5)$  (610 mg, 1.113 mmol) in 50 mL of 2-methoxyethanol. The reaction mixture was stirred at 115 °C for 4 h. After cooling, the solvent was removed under vacuum. The residue was purified by column chromatography on neutral Al<sub>2</sub>O<sub>3</sub>. The crimson-red fraction was eluated with a hexane/ethyl acetate mixture (7:1). The solvent was removed under vacuum, and the residue was crystallized from a CH<sub>2</sub>Cl<sub>2</sub>/hexane mixture. Crimson-red crystalline powder, yield: 570 mg (72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 4.73 (s, 2H, C<sub>5</sub>H<sub>2</sub>), 4.44 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 2.98 (dt, 2H,  $J_{\rm H-H} = 16.7 \text{ Hz}, J_{\rm H-P} = 3.3 \text{ Hz}, CH_2$ , 2.86 (dt, 2H,  $J_{\rm H-H} =$ 16.7 Hz,  $J_{H-P} = 4.6$  Hz,  $CH_2$ ), 1.44 (vt,  $J_{H-P} = 7.0$  Hz, 18H,  $C(CH_3)_3$ , 1.19 (vt,  $J_{H-P} = 6.4$  Hz, 18H,  $C(CH_3)_3$ ). <sup>31</sup> $P\{^{1}H\}$ NMR (162 MHz, CDCl<sub>3</sub>): δ 83.14. IR (CDCl<sub>3</sub>): 1923 cm<sup>-</sup> (v<sub>CO</sub>). Anal. Calcd for C<sub>29</sub>H<sub>47</sub>ClOP<sub>2</sub>Ru<sub>2</sub>: C, 48.97; H, 6.67. Found: C, 48.82; H, 6.39.

Synthesis of { $RuH(CO)['^{Bu}P,CH,P^{Fe}]$ }+{ $BAr^{F}_{4}$ }<sup>-</sup>(3). NaBAr<sup>F</sup><sub>4</sub> (30.0 mg, 0.034 mmol) was added to a solution of 1 (20 mg, 0.03 mmol) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> in a stream of dry hydrogen at room temperature. After 3 min the color turned from dark green to orange, and both NaCl and excess NaBAr<sup>F</sup><sub>4</sub> were filtered off. The solvent was removed by hydrogen stream, and a yelloworange precipitate of 3 was formed. Yellow-orange crystalline powder, quantitative yield. <sup>1</sup>H NMR (600 MHz,  $CD_2Cl_2$ ):  $\delta$ 7.75 (s, 8H, Ar<sup>F</sup>), 7.59 (s, 4H, Ar<sup>F</sup>), 4.45 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.29 (s, 2H, C<sub>5</sub> $H_2$ ), 3.22 (dt, 2H,  $J_{H-H} = 16.4$  Hz,  $J_{H-P} = 3.6$  Hz,  $CH_2$ ), 3.09 (dt, 2H,  $J_{H-H} = 16.4$  Hz,  $J_{H-P} = 3.6$  Hz,  $CH_2$ ), 1.97 (s, 1H, C(1)-H), 1.32 (vt,  $J_{H-P} = 5.5$  Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.24 (vt,  $J_{H-P} = 7.3$  Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>), -26.22 (t, 1H  $J_{H-P} = 15.9$  Hz, RuH). <sup>31</sup>P{<sup>1</sup>H} NMR (243 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  67.9. <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz,  $CD_2Cl_2$ ):  $\delta$  200.69 (s, CO), 161.65 (m,  $J_{C-B}$  = 49.8 Hz,  $C_{ipso}$ -Ar<sup>F</sup>), 134.70 (s,  $C_{ortho}$ -Ar<sup>F</sup>), 128.72 (q,  $J_{C-F} = 32.0$  Hz,  $C_{meta}$ -Ar<sup>F</sup>), 124.50 (q,  $J_{C-F} = 273.0$  Hz,  $CF_3$ -Ar<sup>F</sup>), 117.38 (s,  $C_{para}$ -Ar<sup>F</sup>), 98.51 (t,  $J_{C-P} = 7.7$  Hz, 2,5- $C_5$ H<sub>2</sub>), 71.30 (s,  $C_5H_5$ ), 37.82 (s, C(1)H), 36.64 (t,  $C(CH_3)_3$ ,  $J_{C-P} = 6.4 Hz$ ), 35.37 (t,  $C(CH_3)_3$ ,  $J_{C-P} = 6.4 \text{ Hz}$ ), 28.90 (s,  $C(CH_3)_3$ ), 27.94 (s,  $C(CH_3)_3$ ), 21.16 (t,  $CH_2$ ,  $J_{C-P} = 6.6 \text{ Hz}$ ). IR ( $CH_2Cl_2$ ): 1943  $(v_{CO})$ , 2020 cm<sup>-1</sup>  $(v_{RuH})$ . Anal. Calcd for C<sub>61</sub>H<sub>61</sub>BF<sub>24</sub>FeOP<sub>2</sub>Ru: C, 48.98; H, 4.11. Found: C, 49.35; H, 4.17. A single crystal suitable for X-ray analysis was obtained from CH<sub>2</sub>Cl<sub>2</sub>/hexane at 0−4 °C.

Synthesis of RuH(CO)[ $t^{rBu}P,CH,P^{Ru}$ ]+{BAr<sup>F</sup><sub>4</sub>}<sup>-</sup> (4). NaBAr<sup>F</sup><sub>4</sub> (20.4 mg, 0.023 mmol) was added to a solution of **2** (15 mg, 0.021 mmol) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> in a stream of dry hydrogen at room temperature. After 3 min the color turned from dark red to orange, and both NaCl and excess NaBAr<sup>F</sup><sub>4</sub> were filtered off.

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The solvent was removed by hydrogen stream, and a yelloworange precipitate of **4** was formed. Yellow-orange crystalline powder, quantitative yield. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ 7.73 (s, 8H, Ar<sup>F</sup>), 7.57 (s, 4H, Ar<sup>F</sup>), 4.78 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.61 (s, 2H, C<sub>5</sub>H<sub>2</sub>), 3.13 (dt, 2H,  $J J_{H-H} = 15.5$  Hz,  $J_{H-P} = 4.0$  Hz, CH<sub>2</sub>), 2.98 (dt, 2H,  $J_{H-H} = 15.5$  Hz,  $J_{H-P} = 3.5$  Hz, CH<sub>2</sub>), 2.95 (s, 1H, C(1)-H), 1.40–1.21 (m, 36H, C(CH<sub>3</sub>)<sub>3</sub>), -25.88 (t, 1H  $J_{H-P} = 15.9$  Hz, RuH). <sup>31</sup>P{<sup>1</sup>H} NMR(162 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ 66.9. <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  201.71 (t,  $J_{C-P} =$ 10.1 Hz, CO), 161.58 (m,  $J_{C-F} = 31.4$  Hz,  $C_{meta}$ -Ar<sup>F</sup>), 134.62 (s,  $C_{ottho}$ -Ar<sup>F</sup>), 128.68 (q,  $J_{C-F} = 31.4$  Hz,  $C_{meta}$ -Ar<sup>F</sup>), 97.58 (t,  $J_{C-P} = 9.7$  Hz, 2,5-C<sub>5</sub>H<sub>2</sub>), 73.68 (s, C<sub>5</sub>H<sub>5</sub>), 73.11 (s, 3,4-C<sub>5</sub>H<sub>2</sub>), 44.17 (s, C(1)H), 36.69 (t,  $J_{C-P} = 7.2$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 35.46 (t,  $J_{C-P} = 7.2$  Hz, C(CH<sub>3</sub>)<sub>3</sub>), 28.83 (s, C(CH<sub>3</sub>)<sub>3</sub>), 27.91 (s, C(CH<sub>3</sub>)<sub>3</sub>), 21.14 (t,  $J_{C-P} = 6.4$  Hz, CH<sub>2</sub>). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1945 ( $\nu_{CO}$ ), 2021 cm<sup>-1</sup> ( $\nu_{RuH}$ ).

Synthesis of "*trans*"-RuH(CO)<sub>2</sub>[ $^{rBu}$ P,CH,P<sup>Fe</sup>]<sup>+</sup>{BAr<sup>F</sup><sub>4</sub>}<sup>-</sup> (11). NaBAr<sup>F</sup><sub>4</sub> (30.0 mg, 0.034 mmol) was added to a solution of 1 (20 mg, 0.03 mmol) in 5 mL of  $CH_2Cl_2$  in a stream of dry hydrogen at room temperature. After 3 min the color turned from dark green to orange; then CO was bubbled through the solution until the color turned to dark violet (4-5 min). Excess NaBAr<sup>F</sup><sub>4</sub> and NaCl were filtered off, and the solution was concentrated to 1 mL. Hexane was accurately added, and the solution was kept in a freezer at -18 °C. A strawberry-red, crystalline powder was formed and filtered after 12 h in 82% yield. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.74 (s, 8H, Ar<sup>F</sup>), 7.58 (s,  $^{4}$ H, Ar<sup>F</sup>), 4.63 (d,  $J_{H-P} = 2.0$  Hz, 2H, C<sub>5</sub> $H_2$ ), 4.37 (s, 5H, C<sub>5</sub> $H_5$ ),  $3.15 (dt, 2H, J_{H-H} = 15.1 Hz, J_{H-P} = 4.0 Hz, CH_2), 2.91 (dt, dt, dt)$  $2H, J_{H-H} = 15.1 \text{ Hz}, J_{H-P} = 3.7 \text{ Hz}, CH_2$ , 1.43 (vt,  $J_{H-P} = 7.0$ Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.32 (vt,  $J_{H-P} = 7.6$  Hz, 18H+1H, C(1)-H,  $C(CH_3)_3)$ , -6.02 (dt,  $J_{H-P} = 15.4$  Hz,  $J_{H-H} = 3.1$  Hz, 1H, RuH).  ${}^{31}P{}^{1}H{}$  NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  75.7.  ${}^{13}C{}^{1}H{}$ NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  201.15 (s, CO), 198.51 (s, CO), 163.16 (m,  $J_{C-B} = 50.3$  Hz,  $C_{ipso}$ -Ar<sup>F</sup>), 136.44 (s,  $C_{ortho}$ -Ar<sup>F</sup>), 130.55 (q,  $J_{C-F} = 32.7$  Hz,  $C_{meta}$ -Ar<sup>F</sup>), 126.23 (q,  $J_{C-F} = 273.7$ Hz,  $CF_3$ -Ar<sup>F</sup>), 119.10 (s,  $C_{para}$ -Ar<sup>F</sup>), 107.43 (t,  $J_{C-P} = 6.9$  Hz, 2,5- $C_5$ H<sub>2</sub>), 75.04 (s,  $C_5$ H<sub>5</sub>), 72.34 (s, 3,4- $C_5$ H<sub>2</sub>), 39.06 (t,  $J_{C-P} = 2.2$ 7.2 Hz,  $C(CH_3)_3$ , 37.88 (t,  $J_{C-P} = 6.1$  Hz,  $C(CH_3)_3$ ), 31.41 (s,  $C(CH_3)_3$ , 31.11 (s,  $C(CH_3)_3$ ), 24.27 (t,  $J_{C-P} = 7.0$  Hz,  $CH_2$ ), 8.82 (s, C(1)H). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1958, 2001 ( $\nu_{CO}$ ), 2057 cm  $(\nu_{Ru-H})$ . Anal. Calcd for  $C_{62}H_{61}BF_{24}FeO_2P_2Ru$ : C, 48.87; H, 4.03. Found: C, 48.38; H, 3.93. A single crystal suitable for X-ray analysis was obtained from  $CH_2Cl_2$ /hexane at -18 °C.

Rearrangement of 11 into 13, 15, and 17. The solution of 11 in CD<sub>2</sub>Cl<sub>2</sub> obtained as described above was kept in an NMR tube at room temperature for several days and monitored by NMR spectra. After 24 h, the signals for 11:13:15:17 in a ratio of 10:10:1:6 were observed in the <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra. After 72 h only 15 and 17 in a 2:1 ratio with 15% decomposition products appeared in the  ${}^{31}P{}^{1}H$  NMR spectrum. The solvent was removed under reduced pressure, and the dark green residue was separated by column chromatography on alumina (CH<sub>2</sub>Cl<sub>2</sub>/hexane). Compound  $17^9$  was isolated as a single product in 80% yield (from 1). Complex 15 was fully converted into 17 on Al<sub>2</sub>O<sub>3</sub>. Compound 13: <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ 7.74 (s, 8H,  $Ar^{F}$ ), 7.58 (s, 4H,  $Ar^{F}$ ), 4.63 (d,  $J_{H-P} = 2.0$  Hz, 2H, C<sub>5</sub> $H_2$ ), 4.37 (s, 5H, C<sub>5</sub> $H_5$ ), 3.15 (dt, 2H,  $J_{H-H} = 15.1$  Hz,  $J_{\rm H-P} = 4.0 \,\text{Hz}, \text{C}H_2$ , 2.91 (dt, 2H,  $J_{\rm H-H} = 15.1 \,\text{Hz}, J_{\rm H-P} = 3.7$ Hz,  $CH_2$ ), 2.43 (d,  $J_{H-H} = 1.3$  Hz, 1H, C(1)-H), 1.43 (vt,  $J_{\rm H-P}$  = 7.0 Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.34 (vt,  $J_{\rm H-P}$  = 7.6 Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>), -5.08 (dt,  $J_{H-P} = 17.5$  Hz,  $J_{H-H} = 1.3$  Hz, 1H, RuH). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  75.7. Compound 15: <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 7.74 (s, 8H, Ar<sup>F</sup>), 7.58 (s, 4H, Ar<sup>F</sup>), 4.49 (s, 2H, C<sub>5</sub>H<sub>2</sub>), 4.08 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 3.02 (dt, 2H,  $J_{\rm H-H} = 17.7 \text{ Hz}, J_{\rm H-P} = 3.9 \text{ Hz}, \text{C}H_2$ , 2.71 (dt, 2H,  $J_{\rm H-H} =$ 17.7 Hz,  $J_{H-P} = 4.6$  Hz,  $CH_2$ ), 1.70 (vt,  $J_{H-P} = 7.4$  Hz, 18H,  $C(CH_3)_3$ , 1.36 (vt,  $J_{H-P} = 7.6$  Hz, 18H,  $C(CH_3)_3$ ). <sup>31</sup> $P{^1H}$ NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 111.15. Compound 17:<sup>9</sup> dark green, crystalline powder. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.74 (s, 8H, Ar<sup>F</sup>), 7.58 (s, 4H, Ar<sup>F</sup>), 4.88 (s, 2H, C<sub>5</sub>H<sub>2</sub>), 4.25 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 3.53 (dt, 2H, J<sub>H-H</sub> = 17.0 Hz, J<sub>H-P</sub> = 3.0 Hz, CH<sub>2</sub>), 3.18 (dt, 2H, J<sub>H-H</sub> = 17.0 Hz, J<sub>H-P</sub> = 4.3 Hz, CH<sub>2</sub>), 1.53 (vt, J<sub>H-P</sub> = 7.5 Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 0.94 (vt, J<sub>H-P</sub> = 6.5 Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  98.54. IR (CH<sub>2</sub>Cl<sub>2</sub>): 2003, 1949 cm<sup>-1</sup> ( $\nu$ <sub>CO</sub>).

Synthesis of  $RuH(CO)_2[r^{Bu}P,CH,P^{Ru}]^+ \{BAr_4^F\}^-$  (12). NaBAr<sub>4</sub> (35.0 mg, 0.038 mmol) was added to a solution of 2 (25 mg, 0.035 mmol) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> in a stream of dry hydrogen at room temperature. After 3 min the color turned from dark red to orange. Then CO was bubbled through the solution until the color turned to light yellow (4-5 min). Excess NaBAr<sup>F</sup><sub>4</sub> and NaCl were filtered off, and the solvent was removed under reduced pressure. The spectra were recorded immediately after the reaction because of fast elimination of dihydrogen with formation of 16. Yellow crystalline powder; yield 95%. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 7.76 (s, 8H, Ar<sup>F</sup>), 7.58 (s, 4H, Ar<sup>F</sup>), 4.83 (d,  $J_{H-P} = 2.0$  Hz, 2H, C<sub>5</sub> $H_2$ ), 4.66 (s, 5H, C<sub>5</sub> $H_5$ ), 2.98 (dt, 2H,  $J_{H-H} = 15.3$  Hz,  $J_{H-P} = 4.0$  Hz,  $CH_2$ ), 2.75 (dt, 2H,  $J_{H-H} = 15.3$  Hz,  $J_{H-P} = 3.6$  Hz,  $CH_2$ ), 2.39 (s, 1H, C(1)H), 1.37 (vt,  $J_{H-P} = 4.0 \text{ Hz}, 18\text{H}, C(CH_3)_3), 1.33 \text{ (vt, } J_{H-P} = 4.0 \text{ Hz}, 18\text{H}, C(CH_3)_3), -5.44 \text{ (dt, } J_{H-P} = 15.5 \text{ Hz}, J_{H-H} = 2.4 \text{ Hz}, 18\text{H}, RuH).$  <sup>31</sup>P{<sup>1</sup>H} NMR (243 MHz, CDCl<sub>3</sub>):  $\delta$  75.06. <sup>13</sup>C{<sup>1</sup>H} NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  198.96 (t, CO), 197.27 (t,  $J_{C-P}$  = 11.4 Hz, CO), 161.70 (m,  $J_{C-B} = 48.9$  Hz,  $C_{ipso}$ -Ar<sup>F</sup>), 134.80 (s,  $C_{ortho}$ -Ar<sup>F</sup>), 128.9 (q,  $J_{C-F} = 33.4$  Hz,  $C_{meta}$ -Ar<sup>F</sup>), 124.66 (q,  $J_{C-F} = 269.0$  Hz, Ar<sup>F</sup>), 117.50 (s,  $C_{para}$ -Ar<sup>F</sup>), 105.06 (t,  $J_{C-P} = 7.6$  Hz, 2,5- $C_5$ H<sub>2</sub>), 75.52 (s, 3,4- $C_5$ H<sub>2</sub>), 73.52 (s,  $C_5$ H<sub>5</sub>), 37.54 (t,  $J_{\rm C-P} = 8.2 \text{ Hz}, C(\rm CH_3)_3), 36.14 (t, J_{\rm C-P} = 6.0 \text{ Hz}, C(\rm CH_3)_3),$ 29.90 (s, C(CH<sub>3</sub>)<sub>3</sub>), 29.39 (s, C(CH<sub>3</sub>)<sub>3</sub>), 22.28 (t,  $J_{C-P} = 8.3$  Hz, CH<sub>2</sub>), 17.08 (s, C(1)H). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1960, 2003 (v<sub>CO</sub>), 2057  $cm^{-1}(\nu_{Ru-H})$ . Anal. Calcd for  $C_{62}H_{61}BF_{24}O_2P_2Ru_2$ : C, 47.46; H, 3.92. Found: C, 47.72; H, 3.90. A single crystal suitable for

X-ray analysis was obtained from CH<sub>2</sub>Cl<sub>2</sub>/hexane at 0-4 °C. Synthesis of Ru(CO)<sub>2</sub>[ $^{rBu}$ P,C,P<sup>Ru</sup>]<sup>+</sup>{BAr<sup>F</sup><sub>4</sub>}<sup>-</sup> (16). NaBAr<sup>F</sup><sub>4</sub> (35.0 mg, 0.038 mmol) was added to a solution of 2 (25 mg, 0.035) mmol) in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> in a stream of CO at room temperature, and the color of the reaction mixture turned from dark red to yellow. After 3 min the excess NaBAr<sup>F</sup><sub>4</sub> and NaCl were filtered off through a short alumina column and the solvent was removed under reduced pressure. Yellow crystalline powder, yield: 91%. <sup>1</sup>H NMR (400 MHz,  $CD_2Cl_2$ ):  $\delta$  7.72 (s, 8H, Ar<sup>1</sup> 7.56 (s, 4H,  $Ar^{F}$ ), 5.32 (d, 2H,  $C_{5}H_{2}$ ), 4.90 (s, 5H,  $C_{5}H_{5}$ ), 3.30  $(dt, 2H, J_{H-H} = 16.7 \text{ Hz}, J_{H-P} = 3.9 \text{ Hz}, CH_2), 2.34 (dt, 2H, 2H)$  $J_{H-H} = 16.7 \text{ Hz}, J_{H-P} = 2.7 \text{ Hz}, CH_2), 1.37 (vt, J_{H-P} = 3.3 \text{ Hz}, CH_2)$ 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.35 (vt,  $J_{H-P} = 3.9$  Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>).  ${}^{31}P{}^{1}H{}$  NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  110.87. IR (CH<sub>2</sub>Cl<sub>2</sub>): 2004, 1949 cm<sup>-1</sup> ( $\nu_{CO}$ ). Anal. Calcd for C<sub>62</sub>H<sub>59</sub>BF<sub>24</sub>P<sub>2</sub>O<sub>2</sub>Ru<sub>2</sub>: C, 47.52; H, 3.80; P, 3.95. Found: C, 47.61; H, 3.87; P, 4.16. A single crystal suitable for X-ray analysis was obtained from CH<sub>2</sub>Cl<sub>2</sub>/ hexane at room temperature.

Synthesis of RuH(CO)[<sup>7Bu</sup>P,C,P<sup>Fe</sup>] (5). Complex 1 (100 mg, 0.15 mmol) in 3 mL of THF was added via canula to the precooled, to -78 °C, suspension of 50 mg of LiAlH<sub>4</sub> in 2 mL of THF. The reaction mixture immediately changed color from dark green to light yellow. After stirring for 3 min methanol (0.5 mL) was added dropwise at -78 °C. The mixture was filtered through Celite, and volatiles were removed under reduced pressure to yield 60 mg (63%) of an orange-red solid. <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  4.64 (d, 2H, C<sub>5</sub>H<sub>2</sub>), 3.94 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 2.97 (dt, 2H, J<sub>H-H</sub> = 17.0 Hz, J<sub>H-P</sub> = 3.2 Hz, CH<sub>2</sub>), 2.74 (dt, 2H, J<sub>H-H</sub> = 17.0 Hz, J<sub>H-P</sub> = 4.6 Hz, CH<sub>2</sub>), 1.44 (vt, J<sub>H-P</sub> = 6.4 Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.19 (vt, J<sub>H-P</sub> = 6.3 Hz, 18H, C(CH<sub>3</sub>)<sub>3</sub>), -26.65 (t, J<sub>H-P</sub> = 19.2 Hz, RuH). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  117.88. IR (CH<sub>2</sub>Cl<sub>2</sub>): 1911 cm<sup>-1</sup> ( $\nu_{CO}$ ). Complex **5** was unstable both in solution and in solid state and used immediately for protonation.

**Protonation of RuH**(CO)[ $^{rBu}$ P,C,P<sup>Fe</sup>] (5) with CF<sub>3</sub>COOH. One drop of TFA was added to a solution of 5 in C<sub>6</sub>D<sub>6</sub> in an NMR tube; the spectra were immediately measured and showed the formation of **3**\* in quantitative yield. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ ):  $\delta$  4.45 (s, 5H,  $C_5H_5$ ), 4.37 (s, 2H,  $C_5H_2$ ), 3.05 (dt 2H,  $J_{H-H} = 15.8$  Hz,  $CH_2$ .), 2.76 (dt, 2H,  $J_{H-H} = 15.8$  Hz,  $CH_2$ ), 2.07 (s, 1H, C(1)-H), 1.45 (br s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), 1.02 (br s, 18H, C(CH<sub>3</sub>)<sub>3</sub>), -26.39 (t, 1H,  $J_{H-P} = 16.6$  Hz, RuH). <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz,  $C_6D_6$ ):  $\delta$  67.3. Complex **3**\* was unstable in solution, unlike **3**, possibly because of intolerance of cationic species to CF<sub>3</sub>COO<sup>-</sup> counterion.

X-ray Diffraction Study of 3, 11, 12, and 16. Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART APEX II diffractometer (graphite-monochromated Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å,  $\omega$ -scan technique, T = 100(2) K). APEX II software<sup>22</sup> was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling, and absorption correction, and SHELXTL<sup>23</sup> for space group and structure determination, refinements, graphics, and structure reporting. The structures were solved by direct methods and refined by the full-matrix least-squares technique against  $F^2$  with the anisotropic thermal parameters for all non-hydrogen atoms. The H(1M) and H(1) atoms in structures 3, 11, and 12 were located in difference Fourier synthesis; the remaining hydrogen atoms in

the structures **3**, **11**, **12**, and **16** were placed geometrically. All hydrogen atoms were included in the structure factor calculations in the riding motion approximation. In the crystal structures of **11** and **12**, disordered solvate molecules of hexane and dichloromethane were located with 0.5/0.5 and 0.7/0.3 occupancies, respectively. The *tert*-butyl groups at the P(2) atom in **11** are disordered over two positions with 0.67/0.33 occupancies. In all structures, some of the CF<sub>3</sub> groups in the anion are disordered. In the crystal structure of **16**, there are two crystalographically independent cation—anion pairs with identical geometrical parameters. The principal experimental and crystalographic parameters are presented in Table 3 (see the SI).

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**Supporting Information Available:** Crystal structures for complexes **3**, **11**, **12**, and **16** (in CIF format), NMR and IR spectra of complexes, and results of DFT calculations. This material is available free of charge via the Internet at http:// pubs.acs.org.

<sup>(22)</sup> APEX II software package; Bruker AXS Inc.: Madison, WI, 2005.
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