Ferrocene-Containing (η^{6} -Hexamethylbenzene)ruthenium(II) Methoxycarbenes: Synthesis, Structure, and Electrochemistry

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Received June 9. 1997[®]

The (η^6 -hexamethylbenzene)dichlororuthenium(II) complexes [(η^6 -C₆Me₆)RuCl₂(L)], where $L = PMe_3$ (1), PPh₃ (2), FcPPh₂ (3; Fc = ferrocenvel), and Hdpf (4; Hdpf = (η^5 -C₅H₄PPh₂)Fe(η^5 - C_5H_4COOH), were reacted with terminal alkynes (FcC=CH, Me₃SiC=CH, and PhC=CH) in the presence of NaPF₆ and methanol to give (η^{6} -hexamethylbenzene)chlororuthenium(II) methoxycarbenes $[(\eta^6-C_6Me_6)Ru(=C(OCH_3)CH_2R)Cl(L)]PF_6$ (L/R = PMe₃/Fc (1a), PPh₃/Fc (2a), FcPPh₂/Fc (3a), FcPPh₂/H (3b), FcPPh₂/Ph (3c), Hdpf/Fc (4a), Hdpf/H (4b), and Hdpf/ Ph (4c)). All new compounds were characterized by NMR and IR spectroscopy and also studied by mass spectrometry in liquid matrix. The solid-state structure of 4a·CH₂Cl₂ was determined by single-crystal X-ray diffraction. The electrochemical study of these bi- and trimetallic complexes displayed that upon oxidation, the Ru–ferrocenyl phosphine moiety undergoes a ferrocene/ferrocenium redox process followed by a $Ru(II) \rightarrow Ru(III)$ oxidation which is, however, markedly influenced by the preceding redox change. A redox dissymmetry of carbenes 1a-4c was observed, as these exhibit communication within the Ru-phosphine part while the carbene ferrocenyl group remains isolated and practically unaffected.

Introduction

Incorporating the redox-active ferrocenyl group(s) into an organometallic compound results in the formation of polymetallic species. Apart from being studied as the communicating redox systems,¹ such compounds exhibit unusual electrochemical activation of some molecules.² The conjugated ferrocene derivatives are being tested for second-³ and third-order⁴ optical nonlinearity with the aim of potential application in optical data storage and processing. The use of ferrocenyl ligands in organic synthesis and enantioselective catalysis is also welldocumented.5

As described previously,⁶ the presence of the ferrocenyl group in an arene-ruthenium(II) ferrocenyl-(phenyl)allenylidene complex leads to mesomeric stabilization of this compound. In order to evaluate the mutual modification of the RuII/RuIII and the ferro-

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cene/ferrocenium redox systems according to their possible communication, the ferrocene-containing ruthenium(II) carbenes of the general formula $[(\eta^6-\text{arene}) Ru(=C(OMe)CH_2R)(phosphine)Cl]PF_6$ were studied. These compounds in which the ferrocenyl and RuC_n (*n* = 1) moieties are separated by the methylene group have not been studied yet. Generally, there are two simple ways to prepare ruthenium(II)-ferrocene oligometallic complexes of this type: (a) coordination of the ferrocenyl moiety containing phosphines to ruthenium, (b) transformation of terminal alkynes bearing the ferrocenyl group to carbene complexes. The phosphine complexes can be obtained by a reaction of the $[(\eta^6$ arene)RuCl₂]₂ dimer and the corresponding phosphine. As for the preparation of carbene complexes, it has been shown that the reaction of the arene-ruthenium(II) complexes⁷ [(η^6 -arene)RuCl₂(PR₃)] with terminal alkynes and NaPF₆ in alcohols directly affords alkoxycarbenes under mild conditions.^{8,9} The mechanism of the areneruthenium(II) carbene formation involves the formation of $[L_n Ru(\eta^2 - HC \equiv CR)]$ followed by the $\sigma - \pi$ rearrangement, yielding an unstable σ -vinylidene complex [L_nRu=C=CHR].^{10,11} Formation of the alkoxycarbene then proceeds by addition of alcohol to the electrophilic

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Abstract published in Advance ACS Abstracts, October 15, 1997. (1) Sato, M.; Hayashi, Y.; Kumakura, S.; Shimizu, N.; Katada, M.; Kawata, S. Organometallics 1996, 15, 721 and references therein.

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vinylidene C_{α} carbon. The lower stability of arenevinylidenes toward nucleophiles in comparison with that of their isoelectronic Cp analogues $[(\eta^5-C_5H_5) Ru(=C=CHR')(PR_3)_2|PF_6$ is the consequence of the different electron-donating ability of the $[(\eta^6-\text{arene})\text{Ru} (PR_3)Cl]^+$ and $[(\eta^5-C_5H_5)Ru(PR_3)_2]^+$ moieties, as confirmed by the trends in the Ru^{II}/Ru^{III} redox potentials of $[(\eta^{6}-\text{arene})\text{RuCl}_{2}(\text{PR}_{3})]$ and $[(\eta^{5}-\text{C}_{5}\text{H}_{5})\text{RuCl}(\text{PR}_{3})_{2}].^{9}$ These studies show that the arene-ruthenium derivatives are much more electron deficient than the analogous Cp complexes. On the other hand, the high reactivity of arene-ruthenium(II) vinylidenes can be utilized for the activation of terminal alkynes. The easily accessible complexes $[(\eta^6 - \text{arene})\text{RuCl}_2(\text{PR}_3)]$ (arene = p-cymene or hexamethylbenzene; $PR_3 = PMe_3$ or PPh₃) have been used as catalysts for regioselective syntheses of enol esters,¹² β -oxopropyl esters,¹³ and β -oxoalkyl carbamates,¹⁴ for which analogous ruthenium(II)-cyclopentadienyl derivatives were inactive.

Herein, we report the details of the synthesis and spectral characterization of new (η^6 -hexamethylbenzene)ruthenium(II) methoxycarbenes bearing ferrocenyl unit(s) in the phosphine and/or carbene parts of molecule and also the properties of their parent (η^{6} hexamethylbenzene)ruthenium(II) dichlorophosphine complexes. We also describe the electrochemical behavior of these bimetallic and trimetallic complexes as well as their fragmentation in liquid secondary mass spectra and the crystal structure of $[(\eta^6-C_6Me_6) Ru(=C(OCH_3)CH_2Fc)\{((\eta^5-C_5H_4PPh_2)Fe(\eta^5-C_5H_4COOH)) P_{(Cl)} = P_{6} \cdot CH_{2} Cl_{2} (4a \cdot CH_{2} Cl_{2}).$

Results and Discussion

Syntheses and Characterization. The starting ferrocene-containing phosphine complexes $[(\eta^6-C_6Me_6) RuCl_2(L)$, where $L = FcPPh_2$ (3) and Hdpf (4; Hdpf = $(\eta^{5}-C_{5}H_{4}PPh_{2})Fe(\eta^{5}-C_{5}H_{4}COOH))$, were prepared by the cleavage of the chloro bridges in $[(\eta^6-C_6Me_6)RuCl_2]_2$ on addition of a stoichiometric amount of the corresponding phosphine. These arene-ruthenium complexes and their PMe_3 (1) and PPh_3 (2) analogues were then reacted with terminal alkynes (FcC=CH (**a**), Me₃SiC=CH (**b**), and PhC=CH (c)) in the presence of NaPF₆ in MeOH/ CH_2Cl_2 to give the corresponding methoxycarbenes [(η^6 - C_6Me_6 $Ru(=C(OCH_3)CH_2R)Cl(L)]PF_6$ (L = phosphine, R = Fc (1a, 2a, 3a, 4a), H (3b, 4b), Ph (3c, 4c)) in good vields (Scheme 1). For the preparation of (methoxy)methylcarbenes **3b** and **4b**, the general procedure was used consisting of methanolysis of Si-C bonds in an intermediate formed by the reaction of (trimethysilyl)acetylene.¹⁵ Although the solid benzyl and (ferrocenyl)methyl carbenes seem to be stable in air at room temperature, their methyl analogues exhibit lower stability, especially in solution. This is in accordance with the predominantly steric stabilization of carbenes. The composition and structure of the products were determined by ¹H and ³¹P{¹H} NMR, infrared and mass spectra, and elemental analyses. At room temperature, the ¹H NMR spectra of **3** and **4** show relatively broad lines of the cyclopentadienyl and phenyl protons. Simi-



Fc = ferrocenyl, Hdpf = $(\eta^5 - C_5 H_4 PPh_2)Fe(\eta^5 - C_5 H_4 COOH)$

larly, phosphorus NMR spectra taken at room temperature exhibit the presence of one broad signal with mutually similar coordination shift values: $\Delta_P(3) = 38.4$ and $\Delta_P(\mathbf{4}) = 37.8$ ($\Delta_P = \delta_P(\text{complex}) - \delta_P(\text{free ligand})$; $\delta_{\rm P}({\rm FcPPh}_2) = -15.3, \ \delta_{\rm P}({\rm Hdpf}) = -17.6^{16} \text{ in } {\rm C}[{}^{2}{\rm H}]{\rm Cl}_{3}).$ Respecting the steric requirements of the ferrocenyl phosphines, such broadening of the NMR signals can be attributed to a hindered intramolecular motion, resulting in a dynamic equilibrium of conformers. The temperature-dependent ${}^{31}P{}^{1}H$ NMR spectra of 3 in C[²H]Cl₃ solution revealed the presence of two isomers in *ca.* 4:1 ratio with chemical shifts δ_P 21.5 and 27.4 at 223 K. When the sample is warmed, the signals broaden to the coalescence point, which was found to be within 263-273 K, followed by sharpening of the single signal (δ_P 22.5 at 323 K). The ¹H NMR spectra of carbenes **2a**-**4c** also exhibit broad lines (especially these of the Cp and Ph protons), but no conformer equilibria were observed. Because of the presence of the chiral ruthenium center in carbenes 1a-4c, the methylene protons in the proton NMR become diastereotopic and remarkably anisochronic (the separation of both signals of the AB system $\Delta \delta_{AB}$ is up to 2.07 ppm for 2a). This relatively large separation could be tentatively explained by the presence of strongly anisotropically shielding phenyl and ferrocenyl¹⁷ groups in the phosphine part of the molecules (compare with $\Delta \delta_{AB}$ 0.65 for 1a). In all cases, selective decoupling was used to identify the low-field component of the AB system, which often coincides with the broad and strong signals of the Cp and methoxy protons. For **3a** and **4a**, anisochronicity of the α -protons of carbene cyclopentadienyl was observed while the β -protons remain unresolved. Except for 1a, ¹³C NMR spectra of the carbenes could not be obtained in sufficient quality due to the broadening caused by intramolecular motion which is slow in the NMR scale. Signals arising from

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Table 1. Crystallographic Data for 4a·CH₂Cl₂

formula	$C_{49}H_{53}F_6O_3P_2Cl_3Fe_2Ru$
Μ	1184.97
cryst syst; space group	triclinic; <i>P</i> 1 (No. 2)
a (Å); α (deg)	12.072(1); 104.11(1)
b (Å); β (deg)	14.470(2); 99.663(8)
c (Å); γ (deg)	14.999(2); 93.773(9)
$V(Å^3); Z$	2489.3(5); 2
$D_{\rm c} ({\rm g}\cdot{\rm mL}^{-1})$	1.581
F(000)	1204
cryst size (mm ³)	0.05 imes 0.2 imes 0.3
cryst description	orange-red plate
μ (mm ⁻¹)	1.16
2θ range (deg)	2.8 - 46.0
hkl	$+h, \pm k, \pm l$
no. of diffractions collected; $R(\sigma)^a$	6941; 15.0
no. of unique diffractions	6910
no. of obsd diffractions; $F_0 \ge 4\sigma(F_0)$	3725
standard diffractions	3 monitored every 1 h
variation in standards (%)	2.9
weighting scheme: w_1 , w_2^b	0.0895, 8.6931
no. of params	584
$R_{\rm all}(F), R_{\rm obs}(F)^a$ (%)	17.5, 6.9
$wR_{\text{all}}(F^2), wR_{\text{obs}}(F^2)^a$ (%)	20.8, 16.3
$\mathrm{GOF}_{\mathrm{all}}{}^a$	1.03
$(\Delta/\sigma)_{\rm max}$	0.000
Δho (e·Å ⁻³)	1.11, -0.82

^a $R(F) = \sum (||F_0| - |F_c||)/\sum |F_0|, \ wR(F^2) = \sum [(w(F_0^2 - F_c^2)^2)/(w(F_0^2)^2]^{1/2}, \ \text{GOF} = [\sum (w(F_0^2 - F_c^2)^2)/(N_{\text{diffrs}} - N_{\text{params}})]^{1/2}, \ R(\sigma) = \sum \sigma(F_0^2)/\sum F_o^2.$ ^b Weighting scheme: $w = [\sigma^2(F_0^2) + w_1P^2 + w_2P]^{-1}; P = [\max(F_0^2) + 2F_c^2]/3.$

the Ru=C(OCH₃)CH₂Fc moiety in the ${}^{13}C{}^{1}H$ NMR spectrum of 1a were found within the expected region:⁸ Ru= $C \delta_C 320.7$ (d, ${}^2J_{PC} = 22$ Hz), OCH₃ $\delta_C 67.6$, and $CH_2 \delta_C$ 50.2, as these clearly indicate the presence of carbene. The assignment was supported by DEPT-135. The decrease of electron density on changing the neutral dichloro complex to the cationic carbene also results in a significant downfield shift of the coordinated phosphine signal in the ${}^{31}P{}^{1}H$ NMR spectra. The coordination shift is practically independent of the nature of the substituent R linked to the carbene part, as demonstrated by the similarity of its value for $3\mathbf{a} - \mathbf{c} \Delta_{\mathbf{P}} \approx$ 48 and 4a-c $\Delta_P \approx 50$ (*cf.* Δ_P (2a) = 39.8, δ_P (PPh₃) = -4.1 was obtained under the same conditions). These spectral features are in agreement with the observed electrochemical response of carbenes 1a-4c.

Crystal Structure. A single crystal X-ray diffraction study of 4a·CH₂Cl₂ was carried out to confirm the solidstate structure of carbenes. The crystallographic data are given in Table 1 and the Experimental Section. A listing of selected bond lengths and angles is given in Table 2. As the hexafluorophosphate counterion and solvating dichloromethane do not display any unexceptional features, the organometallic cation is the only interesting part of the present structure. The cation of 4a is chiral due to the presence of four different substituents in a three-legged piano-stool structure; the $(R_{\rm Ru})$ -[$(\eta^6$ -C₆Me₆)Ru(=C(OCH₃)CH₂Fc){($(\eta^5$ -C₅H₄- PPh_2)Fe(η^5 -C₅H₄COOH))-P}(Cl)]⁺ enantiomer was arbitrarily chosen in the refinement (Figure 1, PLA-TON92¹⁸). In the racemic crystal, both enantiomeric cations are joined through double centrosymmetric hydrogen bonds: $O(2) \cdots O(1)^{i} 2.58(2)$ Å, i = -x, -y, 1 - yz which are, however, distorted by the presence of the neighboring dichloromethane molecule: O(2)····Cl(9A)ⁱ 3.44(2) Å, O(1)····Cl(9A) 4.07(2) Å. There are no further significant intermolecular contacts except those at the

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 4a·CH₂Cl₂

$\begin{array}{c} Ru-C(C_6Me_6, av) \\ C_{ar}-C_{ar}(av) \\ C_{ar}-CH_3(av) \end{array}$	2.31(6) 1.41(2) 1.53(1)	$C-C-C(C_6Me_6, av)$	119(2)
Ru-Cl	2.390(3)	Cl-Ru-C(61) Cl-Ru-P(1) P(1)-Ru-C(61)	93.2(4) 85.5(1) 87.0(3)
$\begin{array}{l} Ru-C(61) \\ O(3)-C(61) \\ O(3)-C(62) \\ C(61)-C(63) \\ C(63)-C(71) \\ C-C(Fc, av) \\ Fe-C(av) \end{array}$	$\begin{array}{c} 1.94(1) \\ 1.30(1) \\ 1.46(2) \\ 1.52(2) \\ 1.53(2) \\ 1.38(4) \\ 2.01(3) \end{array}$	$\begin{array}{l} O(3)-C(61)-C(63)\\ C(61)-O(3)-C(62)\\ C(61)-C(63)-C(71)\\ O(3)-C(61)-Ru\\ C(63)-C(61)-Ru\\ C(75)-C(71)-C(63)\\ C(72)-C(71)-C(63)\\ C(72)-C(71)-C(63)\\ C-C-C(Fc, av) \end{array}$	$\begin{array}{c} 117(1)\\ 127(1)\\ 114.4(9)\\ 116.6(8)\\ 126.3(9)\\ 126(1)\\ 127(1)\\ 108(3) \end{array}$
$\begin{array}{l} Ru-P(1) \\ P(1)-C(21) \\ P(1)-C(41) \\ P(1)-C(51) \\ C(31)-C(36) \\ C(36)-O(1) \\ C(36)-O(2) \\ C-C(Fc, av) \\ Fe-C(av) \\ C-C(Ph, av) \end{array}$	$\begin{array}{c} 2.343(3)\\ 1.83(1)\\ 1.82(1)\\ 1.83(1)\\ 1.46(2)\\ 1.24(2)\\ 1.29(2)\\ 1.41(2)\\ 2.04(2)\\ 1.38(2) \end{array}$	$\begin{array}{c} C(21)-P(1)-Ru\\ C(41)-P(1)-Ru\\ C(51)-P(1)-Ru\\ C(21)-P(1)-C(41)\\ C(21)-P(1)-C(51)\\ C(41)-P(1)-C(51)\\ O(1)-C(36)-O(2)\\ O(1)-C(36)-C(31)\\ O(2)-C(36)-C(31)\\ C(32)-C(31)-C(36)\\ C(32)-C(31)-C(36)\\ C(35)-C(31)-C(36)\\ C(35)-C(31)-C(36)\\ C-C-C(Fc, av)\\ C-C-C(Ph, av)\\ \end{array}$	$\begin{array}{c} 112.5(4)\\ 117.5(4)\\ 117.5(3)\\ 103.1(5)\\ 105.9(5)\\ 101.0(5)\\ 123(1)\\ 119(1)\\ 118(1)\\ 118(1)\\ 128(1)\\ 126(1)\\ 108.0(9)\\ 120(1)\\ \end{array}$
P(2)-F(av)	1.47(6)	F-P(2)-F _{cis} (av)	90(4)
C(9A)-Cl(9A) C(9A)-Cl(9B)	1.65(4) 1.79(4)	Cl(9A)-C(9A)-Cl(9B)	108(2)



Figure 1. PLATON plot of the molecule (R_{Ru}) –4a·CH₂Cl₂ at the 30% probability level. The PF₆⁻ anion, the solvating dichloromethane molecule, and all hydrogens are omitted.

van der Waals level. In the molecular structure of the cation, the η^6 -hexamethylbenzene ring and the monodentate ligands are mutually staggered and the η^6 -arene ring is bent about the C(02)–C(05) axis; the dihedral angle of the half planes defined by C(02), C(03), C(04), C(05) and C(05), C(06), C(01), C(02), respectively, is to 8.5(8)°. A similar feature was observed for $[(\eta^6-C_6H_6)-$ RuCl₂(PMePh₂)] and $[(\eta^6-p-MeC_6H_4CHMe_2)RuCl_2-(PMePh_2)].^{19}$ The length of the Ru–Cl bond is close to the mean value found for Ru complexes (2.42(5) Å, 115 structures²⁰) and the Ru–P bond length similar to that of Ru–PPh₂Me (2.40(6) Å, 4 structures; *cf.* Ru–PPh₃ 2.37(4) Å, 59 structures; Ru–PMe₃ 2.31(5) Å, 65 structures). The carbene Ru=C bond (1.94(1) Å) is slightly

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 Table 3. Redox Potentials of Ruthenium Complexes in CH₂Cl₂^a

	$E^{ m Fc}$ [V]			
compound	Fc/Fc ⁺	Ru ^{II} /Ru ^{III}		
1		0.39		
2		0.48		
3	0.03(P) ^b	0.66		
4	0.28(P)	0.68		
1a	0.08(C)	0.90		
2a	0.09(C)	1.12		
3a	0.05(C), 0.27(P)	1.08		
3b	0.22(P)	1.07		
3c	0.27(P)	1.15		
4a	0.06(C), 0.52(P)	1.12		
4b	0.45(P)	1.09		
4 c	0.50(P)	1.16		

^{*a*} All observed redox processes exhibit a peak separation ΔE_p in the range of 75–95 mV and (i_{pa}/i_{pc}) values of unity. Potentials are given relative to ferrocene/ferrocenium, $E^{Fc} = \frac{1}{2}(E_{pa} + E_{pc})$. Derivative cyclic voltammetry was used for E_p and i_p determination. For further experimental details, see Experimental Section. ^{*b*} P and C denotes the ferrocenyl group in the phosphine and carbene parts of molecule, respectively.

shortened in comparison with that of the vinylidene²¹ complex $[(\eta^6-C_6Me_6)Ru(=C(OCH_3)CH=CPh_2)(Me_3P)Cl]$ - PF_6 (1.98 Å) because of the absence of conjugation. The carbene moiety is planar $[\tau(C(62)-O(3)-C(61)-C(63))]$ $= -1(2)^{\circ}$ without any significant difference from the average bond lengths reported for carbenes of the $[L_n Ru = C(OC')C'']$ type (C - C'' 1.50(3) Å, C - O 1.32(2)Å, O-C' 1.47(2) Å; 18 structures²⁰). The carbene ferrocenyl does not show any deformation (the dihedral angle of the least-squares Cp planes 4(2)°) apart from a slight dynamic disorder of the unsubstituted Cp ring along the D_5 axis. The general geometry of carboxyphosphine ferrocenyl remains practically unaffected by coordination (the dihedral angle of Cp ring planes 5.6(9)°, C-P-C angles similar to those of noncoordinated Hdpf¹⁶). The only significant difference is the relative conformation of the carboxy and diphenylphosphino groups, which are *anti*-eclipsed with the torsion angle $\tau(P(1)-CE(1)-CE(2)-C(36)) -148.1(5)^\circ$; in contrast, noncoordinated Hdpf occupies a halfway anti-conformation with the τ value of *ca.* -162° . As the rotational barrier along the D_5 axis is known to be low, such changes are invoked most likely by crystal packing effects, the H bond formation being one of the most significant.

Electrochemistry. For all compounds, the electrochemical study revealed that all observed redox processes are one-electron and reversible processes at the scan rate of $1 \text{ V} \cdot \text{s}^{-1}$, as indicated by the (i_{pa}/i_{pc}) ratios of unity and the ΔE_p peak separations in the range of 75-95 mV. The redox potentials E^{Fc} given relative to ferrocene/ferrocenium²² are summarized in Table 3. The cyclic voltammograms of the starting chloro complexes 1 and 2 display only one wave from the Ru^{II}/Ru^{III} redox couple. The easier oxidation of 1 in comparison to 2 is in accordance with the higher electron-donating ability of the PMe₃ ligand. The presence of ferrocenyl-bearing phosphines in complexes 3 and 4, reflected by the

appearance of the additional wave of the Fc/Fc⁺ couple, strongly modifies the properties of both electrochemically active parts of the complex. First, the presence of ferrocenyl phosphine causes a relative increase of the Ru^{II}/Ru^{III} potential and, simultaneously, the decrease of the ferrocene/ferrocenium potential. For illustration, $E^{\rm Fc}({\rm FcPPh}_2) = 0.11 \text{ V with } \Delta E_{\rm p} = 80 \text{ mV and } (i_{\rm pa}/i_{\rm pc}) \approx$ 0.4 at the same conditions; for Hdpf, only the anodic peak potential could be detected at the scan rate of 1 $V \cdot s^{-1}$, $E_{pa}^{Fc} = 0.39$ V. Second, there is an apparent contradiction with the expected trend, *i.e.*, the decrease of the electron density in the ligand moiety on dative bond formation, which causes an increase of the potential of the ligand-centered redox process. This common trend could be illustrated by the potentials of the following (diphenylphosphino)ferrocene complexes: $[(FcPPh_2)M(CO)_5], M = Mo E^{Fc} = 0.27 V; W E^{Fc} = 0.29$ V; while for noncoordinated FcPPh₂, $E^{Fc} = 0.11$ V.²³ Such an unexpected electrochemical response for 3 and 4 could be attributed to a significant contribution of the Ru \leftarrow P π -back-donation, resulting in a decrease of the electron-withdrawing properties of the diphenylphosphino group and, in this way, relative increase of the electron density within the ferrocenyl moiety. At a higher potential, the ferrocenium formed in the first oxidative step undergoes a successive rutheniumcentered oxidation. However, the presence of the strongly electron-withdrawing ferrocenium makes this step more difficult in comparison with simple phosphines containing complexes 1 and 2, as indicated by the shift to higher potentials. Thus, by modification of the phosphine substituent, the Ru^{II}/Ru^{III} potential shifted to a higher value although, taking into account the electron-donating ability of the ferrocenyl group, the potential could be a priori expected between those of 1 and 2. The coordination also stabilizes both ferrocenyl phosphines toward subsequent reactions¹⁶ of the ferricinum species yielding phosphine oxides. While free ferrocenyl phosphines exhibit quasi-reversible waves reflecting the subsequent decomposition of the generated ferrocenium, the values of $(i_{\rm pa}/\bar{i}_{\rm pc}) \approx 1$ observed for the phosphinecentered redox step indicate reversible ferroceneferrocenium processes in the case of 3, 4, 3a-c, and 4ac. An analogous stabilization has been reported for (diphenylphosphino)ferrocene complexes of molybdenum and tungsten (vide infra). Similarly, when not stabilized by the formation of stable complexes such as $[M(dppf-P,P')Cl_2], M = Pd, Pt,^{24}$ free 1,1'-bis(diphenylphosphino)ferrocene (dppf) is oxidized to ferrocenium and immediately converted to protonated and higher oxidized species.²⁵

The change of the electrochemical response of the carbene complexes in comparison to the neutral parent chloro complexes is consistent with generation of cationic species (Figure 2). The electron density decrease makes oxidation of Ru^{II} markedly more difficult, as documented by the positive shift of about 0.5 V for the ruthenium-centered oxidation. This change also affects the phosphine part of the molecule, as manifested by the anodic shift of approximately +0.2 V for the Fc/Fc⁺

⁽²¹⁾ Structure VOYDOC in Cambridge Crystallographic Data Centre; for reference see: Allen, F. H.; Kennard, O. *Chem. Design Automat. News* **1993**, *8*, 1, 31–37. (22) $E^{\text{SCE}} = E^{\text{Fc}} + E^{\text{SCE}}(\text{FcH/FcH}^+)$; $E^{\text{SCE}}(\text{FcH/FcH}^+) = +0.46$ V in

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Table 4. Mass Spectrometric Characteristics of Carbenes $[(\eta^6-HMB)Ru(=C(OCH_3)CH_2R)(L)Cl]PF_6^a$

compound (L/R)	1a (PMe ₃ /Fc)	2a (PPh ₃ /Fc)	3a (FcPPh ₂ /Fc)	3b (FcPPh ₂ /H)	3c (FcPPh ₂ /Ph)	4a (Hdpf/Fc)	4b (Hdpf/H)	4c (Hdpf/Ph)
[cation] ⁺	617(100)	803(17)	911(100)	727(11)	803(100)	955(79)	771(7)	847(94)
[cation – HCl] ⁺	581(2)	weak	875(2)	weak	767(3)	weak		811(3)
[cation – HMB – HCl] ⁺	419(11)	605(8)	713(22)		605(10)	757(21)		649(42)
$[cation - C(OCH_3)CH_2R]^+$	375(40)	561(9)	669(10)	669(12)	669(3)	713(6)	713(26)	713(3)
$[cation - C(OCH_3)CH_2R - HCl]^+$	<350	525(13)	633(6)	633(3)	633(3)	677(40)	677(46)	677(16)
$[cation - L]^+$	541(3)	541(9)	541(42)	357(14)	433(48)	541(100)	357(12)	433(100)
$[cation - L - HCl]^+$		505(6)	505(10)	weak	397(18)	505(29)	321(22)	397(51)
L ⁺	<350	<350	370(97)	370(100)	370(81)	414(29)	414(100)	414(35)
$[LCH_2R]^+$	<350	461(100)	569(29)					
[cation – CpFe – HMB – Cl] ⁺	<350	485(16)	593(45)	weak	485(19)	637(25)		
$[cation - C_6H_5O_2Fe - HMB - Cl]^+$						593(14)		485(24)
$[cation - CpFe - C(OCH_3)CH_2R - HCl]^+$	<350	<350	513(18)	513(12)	513(8)			
$[cation - C_6H_5O_2Fe - C(OCH_3)CH_2R - HCl]^+$						513(21)	513(54)	513(14)
other					641(8) ^b	887(22) ^c		779(8) ^c

^{*a*} LSIMS data obtained in a 3-nitrobenzyl alcohol matrix. The signals with m/z > 350 only are listed as m/z(relative intensity). HMB = hexamethylbenzene, L = phosphine. ^{*b*} [cation - HMB]⁺. ^{*c*} [cation - 68]⁺, possible elimination of HCl and MeOH.



Figure 2. Cyclic voltammetric response of **4** (broken line) and **4a** (full line). C, P, and Ru denote carbene ferrocenyl, phosphine ferrocenyl, and ruthenium-centered redox processes, respectively (circled for **4a**).

potential. This is most likely caused by an electrondensity transfer from phosphine to ruthenium, which cannot be compensated by back-donation from the now electron-deficient metal. Similar trends in the Fc/Fc⁺ potential were observed in the case of the (diphenylphosphino)ferrocene carbonyl complexes of molybdenum and tungsten mentioned above, in which the contribution of the back-donation from the metal to phosphorus could be expected to be weak due to the presence of five good π -accepting carbonyl ligands. Moreover, replacement of the electron-withdrawing ethynyl group by an electron-donating alkyl returns the carbene Fc/Fc+ potential in 1a, 2a, 3a, and 4a to values close to those of unsubstituted ferrocene (*cf.* FcC=CH $E^{Fc} = 0.16$ V, $\Delta E_{\rm p} = 75$ mV, $i_{\rm pa}/i_{\rm pc} = 1.0$ under the same conditions). These potentials are practically unaffected by changes on the metal center. Likewise, the Ru^{II}/Ru^{III} potentials exhibit only a small variation on changing the substituent in the carbene part, as indicated by the trends in 3a-c and 4a-c. These facts clearly imply an interruption of electronic communication, except for simple inductive effects, between L_nRu=C and the carbene substituent R (Ru=C(OCH₃)CH₂R) on introduction of a CH₂ spacer.

Mass Spectrometry. The positive-mode secondary

ion mass spectra of the complexed salts **1a**, **2a**, **3a**–**c**, and 4a-c exclusively exhibit the signals of the free organometallic cations and their fragment ions, most likely owing to the dissociation of the ionic carbenes dissolved in the matrix. Nevertheless, the presence of the hexafluorophosphate counterion is obvious from the presence of weak signals due to the formation of clusters $[cation_2, PF_6^-]^+$. In general, the cations undergo fragmentation by splitting of ruthenium-bonded ligands, *i.e.*, the carbene part, hexamethylbenzene, or phosphine, together or without the elimination of HCl (Table 4). While fragment ions corresponding to the loss of the phosphine or carbene part with or without concurrent elimination of HCl are easily observable; the peaks corresponding to the loss of C₆Me₆ or HCl are weak or not observed at all. On the other hand, the simultaneous loss of C6Me6 and HCl results in peaks of considerable intensity, with the exception of methyl carbenes 3b and 4b. All spectra also display the presence of positively charged free phosphines. In the case of **2a** and **3a**, further peaks appear in the spectra which correspond to phosphonium ions resulting by the migration of the carbene substituent (RCH₂ in [L_nRu- $(=C(OCH_3)CH_2R)]^+$) to phosphine phosphorus. It is worth noting that the presence of the ferrocene skeleton in all cases leads to the occurrence of less common ionic species in the spectra. Their formation involves elimination of cyclopentadienyl-iron ($[C_5H_5Fe]^+$) or carboxycyclopentadienyl-iron ($[C_6H_5O_2Fe]^+$) fragments arising from phosphine or carbene ferrocenyls.

The mass spectra of dichloro complexes **3** and **4** exhibit positively charged molecular ions and fragments $[M - nCl]^+$ (n = 1, 2). Although the loss of the phosphine molecule has not been observed here, the charged phosphines, $[FcPPh_2]^+$ and $[Hdpf]^+$, appear as the most intense peaks in the spectra (for low-resolution mass spectral data, see Experimental Section). A further notable feature similar to that in the carbenes is the presence of the ionic species m/z 513 due to the simultaneous loss of two chlorine atoms and $[C_5H_5Fe]^+$ and $[C_6H_5O_2Fe]^+$ for **3** and **4**.

Concluding Remarks

We described the syntheses of several new ferrocenylsubstituted ruthenium(II) carbenes. These compounds were studied with respect to their structure and electronic properties by multinuclear NMR spectroscopy and electrochemistry in solution and by single-crystal X-ray diffraction in the solid state. From the electrochemical behavior of the ferrocenyl phosphines bearing (η^6 -hexamethylbenzene)chlororuthenium(II) methoxycarbenes and their parent (η^6 -hexamethylbenzene)dichlororuthenium(II) complexes, it follows that there is no electronic communication between the L_nRu=C moiety and the carbene substituent, excluding inductive effects. On the other hand, the presence of the oxidized phosphine ligand (formation of *P*-coordinated ferrocenium precedes the $Ru^{II} \rightarrow Ru^{III}$ oxidation) results in a significant electron density lowering at the central atom. Such a modification of the electronic properties of the metal center in catalytically important organometallic compounds by changing the oxidation state of ligand(s) might be used for fine "tuning" their catalytic properties.

Experimental Section

General Considerations. All experiments were carried out in an atmosphere of argon or nitrogen using Schlenk techniques. The solvents were dried and deoxygenated by standard procedures. ¹H (200.13 MHz), ³¹P{¹H} (81.02 MHz), and ${}^{13}C{}^{1}H{}$ (50.33 MHz) NMR spectra were recorded on a Bruker DPX200 spectrometer at 296 K with external tetramethylsilane (¹H, $^{\hat{1}3}$ C) and external 85% aqueous H₃PO₄ (³¹P) as the standards. Liquid secondary-ion mass spectral (LSIMS) data were obtained on a VG ZabSpec spectrometer (CRMPO center, University of Rennes) operating in a positive-ion mode using CsI as the primary ion source and 3-nitrobenzyl alcohol as the matrix. For high-resolution measurements (HRMS), poly(ethylene glycol) was used as the mass scale calibrant. IR spectra were recorded on a Nicolet 205 spectrometer in KBr pellets. Cyclic voltammograms were measured in an argon atmosphere with 1×10^{-3} M dichloromethane solutions containing 0.1 M Bu₄NPF₆ as the supporting electrolyte at the scan rate of 1 V·s⁻¹. The measurements were carried out using a potentiostat (model 263, EG&G Princeton Applied Research) connected to an oscilloscope (Nicolet 310), a wave form generator (Hewlett-Packard 33120A), and a selective amplifier (model 189, EG&G Princeton Applied Research) with platinum discs of 0.4 mm diameter as the working and auxiliary electrodes and a saturated calomel electrode as the reference. The potentials are given relative to ferrocene/ferrocenium; a calibration cyclic voltammogram of ferrocene was registered before each measurement. Elementary analyses were performed by the CNRS Service Central d'Analyses (Vernaison, France). $[(\eta^6-C_6Me_6)Ru(\mu-Cl)Cl]_2,^{26} [(\eta^6-C_6Me_6)Ru(L)Cl_2]^{27} (L)$ = PMe_3 (1), PPh_3 (2)), $FcC \equiv CH$, ²⁸ $FcPPh_2$, ²⁹ and $Hdpf^{16}$ were prepared according to the published procedures.

Preparation of $(\eta^6$ -Hexamethylbenzene)RuCl₂(phosphine) Complexes, $[(\eta^6-C_6Me_6)Ru(FcPPh_2)Cl_2]$ (3). To a stirred solution of $[(\eta^6-C_6Me_6)Ru(\mu-Cl)Cl]_2$ (0.667 g, 1.00 mmol) in dichloromethane (50 mL), FcPPh₂ (0.750 g, 2.03 mmol) was added in one portion and the mixture was stirred for 90 min at room temperature. After evaporation under reduced pressure, the product was washed with diethyl ether (25 mL) and pentane (2 \times 25 mL) and dried *in vacuo* to give **3** (1.283 g, 91%) as an orange-red solid. ¹H NMR (C[²H]Cl₃): δ 1.75 (d, ${}^{4}J_{\rm PH} = 0.5$ Hz, 18 H, C₆Me₆), 3.78 (s, 5 H, C₅H₅), 4.42 (br s, 2 H, C_5H_4), 4.56 (br s, 2 H, C_5H_4), 7.34–7.46 (m, 6 H, PPh₂), 7.85-8.01 (m, 4 H, PPh₂). ${}^{31}P{}^{1}H{}$ NMR (C[${}^{2}H{}$]Cl₃): δ 22.3 (br s). IR (cm⁻¹): ν (CH) 3049 (w), 2908 (w); δ_s (CH₃) 1383 (m); Fc 1096 (m), 1002 (m); PPh₂ 470 (s, composed). Anal. Calcd for C₃₄H₃₇PCl₂FeRu: C, 57.97; H, 5.29; P, 4.40. Found: C, 58.07; H, 5.41 P, 4.20. HR LSIMS: m/z [C₃₄H₃₇PCl₂FeRu]⁺ (M⁺) calcd 704.0409, found 704.039; [C₃₄H₃₇PClFeRu]⁺ ([M -Cl]⁺), calcd 669.0723, found 669.072. LSIMS: *m*/*z* (relative intensity) 704 (6, M⁺), 669 (25, [M - Cl]⁺), 633 (3, [M - 2Cl]⁺), 513 (15, $[M - 2Cl - C_5H_5Fe]^+$), 370 (100, $[FcPPh_2]^+$).

 $[(\eta^{6}-C_{6}Me_{6})Ru(Hdpf-P)Cl_{2}]$ (4). Starting from $[(\eta^{6}-C_{6}Me_{6})-$ Ru(µ-Cl)Cl]₂ (0.667 g, 1.00 mmol) and Hdpf (0.829 g, 2.00 mmol), the same procedure as for 3 yielded 4 (1.470 g, 98%) as an orange-red solid. ¹H NMR (C[²H]Cl₃): δ 1.75 (s, 18 H, C₆Me₆), 3.74 (s, 2 H, C₅H₄), 4.50 (s, 4 H, C₅H₄), 4.60 (s, 2 H, C₅H₄), 7.33-7.52 (br s, 6 H, PPh₂), 7.78-7.98 (br s, 4 H, PPh₂). ³¹P{¹H} NMR (C[²H]Cl₃): δ 20.2 (br s). IR (cm⁻¹): ν (CH) 3050 (w), 2982 (w); ν (C=O) 1712 (m), 1686 (s); δ_s (CH₃) 1385 (m); Fc 1096 (m), 1035 (m); PPh₂ 490 (s, composed). Anal. Calcd for C35H37O2PCl2FeRu: C, 56.17; H, 4.98; P, 4.14. Found: C, 55.89; H, 4.90; P, 4.01. HR LSIMS: *m*/*z* [C₃₅H₃₇O₂PCl₂FeRu]⁺ (M⁺) calcd 748.0308, found 748.032; $[C_{35}H_{37}O_2PClFeRu]^+$ ([M - Cl]⁺), calcd 713.0621, found 713.060. LSIMS: *m*/*z* (relative intensity) 748 (6, M^+), 713 (35, $[M - Cl]^+$), 677 (66, $[M - 2Cl]^+$), 513 (15, $[M - 2Cl - C_6H_5O_2Fe]^+$), 414 (100, $[Hdpf]^+$).

General Procedure for Preparation of Carbenes. The starting ruthenium(II) complex $[(\eta^6-C_6Me_6)RuCl_2(phosphine)]$ (0.5 mmol) and NaPF_6 (0.5 mmol or slight excess) were dissolved in methanol (25 mL) and dichloromethane (25 mL; except for 1a), and an excess of alkyne was added. The mixture was stirred at room temperature for 90 min (the progress of reaction causes color lightening), and the resulting solution was evaporated under reduced pressure. After the solid was washed with diethyl ether (3 \times 20 mL; removal of unreacted alkyne) and dried in vacuo, the solid residue was dissolved in dichloromethane (10 mL) and the solution filtered via cannula to remove NaCl. After addition of pentane (40 mL) to the filtrate, the biphasic mixture was left to crystallize on diffusion at -20 °C for several days. Decantation of the solvent mixture followed by washing with pentane (20 mL) and drying in vacuo afforded solid carbenes.

 $[(\eta^6-C_6Me_6)Ru(=C(OCH_3)CH_2Fc)(PMe_3)(Cl)]$ (1a). 1 (206) mg, 0.50 mmol), NaPF₆ (86 mg, 0.51 mmol) and FcC=CH (316 mg, 1.50 mmol) gave 1a (310 mg, 81%) as ruby-red crystals. The reaction was carried out in methanol (25 mL) without addition of dichloromethane. ¹H NMR (C[²H]Cl₃): δ 1.47 (d, $^{2}J_{\rm PH} = 10.6$ Hz, 9 H, PMe₃), 2.04 (s, 18 H, C₆Me₆), 4.20 (br m, 2 H, C₅H₄), 4.22 (d, ${}^{2}J_{HH} = 12.6$ Hz, 1 H, AB CH₂), 4.23 (s, 5 H, C₅H₅), 4.31 (s, 2 H, C₅H₄), 4.69 (s, 3 H, OMe), 4.87 (d, ²J_{HH} = 12.6 Hz, 1 H, AB CH₂). ³¹P{¹H} NMR (C[²H]Cl₃): δ -143.1 (sept, ${}^{1}J_{PF} = 712$ Hz, PF_{6}^{-}), 9.1 (s, PMe_{3}). ${}^{13}C{}^{1}H{}$ NMR (C[${}^{2}H{}$]-Cl₃): δ 16.2 (d, ¹*J*_{PC} = 34 Hz, P*Me*₃), 16.8 (s, C₆*Me*₆), 50.2 (s, *C*H₂), 67.6 (s, O*Me*), 68.9 (d, ${}^{2}J_{PC} = 31$ Hz, C₅H₄, C_a), 70.1 (s, C_5H_5), 72.2 (s, C_5H_4 , C_β), 78.5 (d, ${}^1J_{PC} = 86$ Hz, C_5H_4 , C_{ipso}), 107.6 (d, ${}^{2}J_{PC} = 2$ Hz, $C_{6}Me_{6}$), 320.7 (d, ${}^{2}J_{PC} = 22$ Hz, Ru=C). IR (cm⁻¹): ν (CH) 3094 (w), 2920 (w); δ_s (CH₃) 1385 (m); ν (C-O) 1275 (s); Fc 1052 (m), 954 (m); PF_6^- 839 (s); PPh_2 482 (s). Anal. Calcd for C₂₈H₄₁OF₆P₂ClFeRu: C, 44.14; H, 5.42; P, 8.13. Found: C, 44.64; H, 5.40; P, 7.87. HR LSIMS: m/z $[C_{28}H_{41}OPClFeRu]^+$ ($[M - PF_6]^+$), calcd 617.0983, found 617.095.

 $[(\eta^6-C_6Me_6)Ru(=C(OCH_3)CH_2Fc)(PPh_3)(Cl)]$ (2a). 2 (299) mg, 0.50 mmol), NaPF₆ (86 mg, 0.51 mmol) and FcC=CH (210 mg, 1.00 mmol) gave 2a (422 mg, 89%) as rusty-brown needles. ¹H NMR (C[²H]Cl₃): δ 1.76 (s, 18 H, C₆Me₆), 2.37 (d, ²J_{HH} = 12.3 Hz, 1 H, AB CH₂), 4.01 (s, 5 H, C₅H₅), 4.12 (m, 2 H, C₅H₄, H_{β}), 4.14 (m, 1 H, C₅H₄, H_{α}), 4.44 (d, ² J_{HH} = 12.3 Hz, 1 H, AB CH_2), 4.65 (m, 1 H, C₅H₄, H_{α}), 4.66 (s, 3 H, OMe), 7.46-7.62 (m, 15 H, PPh₃). ${}^{31}P{}^{1}H$ NMR (C[${}^{2}H$]Cl₃): δ -143.0 (sept, ${}^{1}J_{\text{PF}} = 712 \text{ Hz}, PF_{6}^{-}), 35.7 \text{ (s, } PPh_{3}). \text{ IR (cm}^{-1}): \nu(\text{CH}) 3056$ (w), 2923 (w); δ_s (CH₃) 1385 (m); ν (C–O) 1287 (s); Fc 1095 (m), 1002 (m); PF_6^- 839 (s); PPh_3 491–558 (composed s). Anal. Calcd for C43H47OF6P2ClFeRu: C, 54.47; H, 4.00. Found: C,

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54.26; H, 4.28. HR LSIMS: m/z [C₄₃H₄₇OPClFeRu]⁺ ([M – PF₆]⁺), calcd 803.1457, found 803.145.

[(η⁶-C₆Me₆)Ru(=C(OCH₃)CH₂Fc)(PPh₂Fc)(Cl)] (3a). 3 (353 mg, 0.50 mmol), NaPF₆ (84 mg, 0.50 mmol), and FcC=CH (212 mg, 1.01 mmol) gave **3a** (439 mg, 83%) as a brown solid. ¹H NMR (C[²H]Cl₃): δ 1.74 (s, 18 H, C₆Me₆), 2.21 (d, ²J_{HH} = 12.6 Hz, 1 H, AB CH₂), 4.00 (s, 10 H, C₅H₅), 4.03 (d, 1 H, AB CH₂, identified by selective decoupling), 4.05 (br m, 2 H, C₅H₄), 4.10 (m, 2 H, C₅H₄), 4.63 (s, 3 H, OMe), 4.47–4.82 (br m, 4 H, C₅H₄), 7.54–8.02 (br m, 10 H, PPh₂). ³¹P{¹H} NMR (C[²H]Cl₃): δ –143.0 (sept, ¹J_{PF} = 712 Hz, PF₆⁻), 32.5 (s, PPh₂Fc). IR (cm⁻¹): ν(CH) 3092 (w), 2922 (w); δ_s(CH₃) 1386 (m); ν(C–O) 1299, 1262 (s); Fc 1110 (m), 1003 (m); PF₆⁻ 840 (s); PPh₂ 491 (s), 475 (s). Anal. Calcd for C₄₇H₅₁OF₆P₂ClFe₂Ru: C, 53.45; H, 4.87; P, 5.87. Found: C, 53.02; H, 4.86; P, 5.74. HR LSIMS: m/z [C₄₇H₅₁OPClFe₂Ru]⁺ ([M – PF₆]⁺) calcd 911.1123, found 911.114.

[(η⁶-C₆Me₆)Ru(=C(OCH₃)CH₃)(PPh₂Fc)(Cl)] (3b). 3 (354 mg, 0.50 mmol), NaPF₆ (86 mg, 0.51 mmol), and Me₃SiC=CH (0.20 mL, 1.4 mmol) gave **3b** (298 mg, 68%) as a rusty-orange solid. ¹H NMR (C[²H]₂Cl₂): δ 1.87 (s, 18 H, C₆Me₆), 2.25 (br s, 3 H, Ru=CCH₃), 4.00 (s, 5 H, C₅H₅), 4.37 (s, 3 H, OMe), 4.55 (br s, 2 H, C₅H₄), 4.66 (br s, 2 H, C₅H₄), 7.46–7.98 (br m, 10 H, PPh₂). ³¹P{¹H} NMR (C[²H]₂Cl₂): δ -143.2 (sept, ¹J_{PF} = 711 Hz, PF₆⁻), 32.8 (br s, PPh₂Fc). IR (cm⁻¹): ν(CH) 3048 (w), 2915 (w); δ₃(CH₃) 1385 (m); ν(C–O) 1282 (m); Fc 1098 (m), 1001 (m); PF₆⁻ 839 (s); PPh₂ 473–518 (s, composed). HR LSIMS: m/z [C₃₇H₄₃OPClFeRu]⁺ ([M – PF₆]⁺) calcd 727.1142, found 727.114. The instability of the compound at ambient conditions did not permit us to obtain correct microanalytical results.

 $[(\eta^{6}-C_{6}Me_{6})Ru(=C(OCH_{3})CH_{2}Ph)(PPh_{2}Fc)(Cl)]$ (3c). 3 (355 mg, 0.50 mmol), NaPF₆ (87 mg, 0.52 mmol), and PhC=CH (0.15 mL, 1.4 mmol) gave 3c (412 mg, 86%) as a rusty-red microcrystalline solid. ¹H NMR (C[²H]Cl₃): δ 1.77 (s, 18 H, C_6Me_6), 2.51 (d, ²J_{HH} = 13.2 Hz, 1 H, AB CH₂), 3.92 (s, 1 H, C_5H_4), 3.93 (s, 5 H, C_5H_5), 4.45 (s, 1 H, C_5H_4), 4.52 (d, ² $J_{HH} =$ 13.2 Hz, 1 H, AB CH₂), 4.53 (s, 3 H, OMe), 4.66 (s, 1 H, C₅H₄), 4.94 (br s, 1 H, C₅H₄), 7.01-7.11 (m, 2 H, CH₂Ph), 7.21-7.31 (m, 3 H, CH₂Ph), 7.55-8.11 (br m, 10 H, PPh₂). ³¹P{¹H} NMR (C[²H]Cl₃): δ -143.1 (sept, ¹J_{PF} = 712 Hz, *P*F₆⁻), 32.7 (s, *P*Ph₂Fc). IR (cm⁻¹): ν (CH) 3057 (w), 2924 (w); δ_s (CH₃) 1386 (m); ν (C–O) 1301 (s), 1262 (s); Fc 1096 (m), 1003 (m); PF₆⁻ 839 (s); PPh₂ 491 (s), 477 (s). Anal. Calcd for C₄₃H₄₇OF₆P₂-ClFeRu: C, 54.47; H, 4.00; P, 6.53. Found: C, 54.26; H, 4.09; P, 6.55. HR LSIMS: $m/z [C_{43}H_{47}OPClFeRu]^+ ([M - PF_6]^+)$ calcd 803.1457, found 803.144.

[(η⁶-C₆Me₆)Ru(=C(OCH₃)CH₂Fc)(Hdpf-*P*)(Cl)] (4a). 4 (375 mg, 0.50 mmol), NaPF₆ (86 mg, 0.51 mmol), and FcC=CH (210 mg, 1.00 mmol) gave 4a (479 mg, 87%) as brown needles. ¹H NMR (C[²H]₂Cl₂): δ 1.73 (s, 18 H, C₆*Me*₆), 2.17 (d, ²*J*_{HH} = 12.8 Hz, 1 H, AB C*H*₂), 4.03 (s, 5 H, C₅*H*₅), 4.04 (d, 1 H, AB C*H*₂, identified by selective decoupling), 4.08 (s, 2 H, C₅*H*₄), 4.16 (s, 2 H, C₅*H*₄), 4.49 (s, 3 H, O*Me*), 4.42–4.82 (br m, 8 H, C₅*H*₄), 7.35–8.15 (br m, 10 H, P*Ph*₂). ³¹P{¹H} NMR (C[²H]₂-Cl₂): δ –143.3 (sept, ¹*J*_{PF} = 711 Hz, *P*F₆⁻), 31.8 (br s, *Hdpf*). IR (cm⁻¹): *ν*(CH) 3094 (w), 2925 (w); *ν*(C=O) 1719, 1677; δ_{s} (CH₃) 1386 (m); *ν*(C=O) 1292, 1270 (s); Fc 1096 (m), 1040 (s), 1002 (m); PF₆⁻ 841 (s); PPh₂ 484 (s). Anal. Calcd for C₄₈H₅₁O₃F₆P₂ClFe₂Ru: C, 52.41; H, 4.67; P, 5.63. Found: C, 52.25; H, 4.65; P, 5.55. HR LSIMS: *m*/*z* [C₄₈H₅₁O₃PClFe₂-Ru]⁺ ([M – PF₆]⁺) calcd 955.1022, found 955.103.

[(η^{6} -C₆Me₆)Ru(=C(OCH₃)CH₃)(Hdpf-*P*)(Cl)] (4b). 4 (375 mg, 0.50 mmol), NaPF₆ (86 mg, 0.51 mmol), and Me₃SiC≡CH (0.20 mL, 1.4 mmol) gave 4b (342 mg, 75%) as a rusty-orange solid. ¹H NMR (C[²H]₂Cl₂): δ 1.85 (s, 18 H, C₆Me₆), 2.38 (br s, 3 H, Ru=CCH₃), 4.11 (br m, 2 H, C₅H₄), 4.33 (s, 2 H, C₅H₄), 4.53 (s, 3 H, OMe), 4.64 (br s, 1 H, C₅H₄), 4.70 (br s, 1 H, C₅H₄),

4.84 (br s, 2 H, C₅*H*₄), 7.48–7.82 (br m, 10 H, P*Ph*₂). ³¹P{¹H} NMR (C[²H]₂Cl₂): δ –143.2 (sept, ¹*J*_{PF} = 711 Hz, *P*F₆⁻), 32.3 (br s, *Hdpf*). IR (cm⁻¹): *v*(CH) 3055 (w), 2918 (w); *v*(C=O) 1712 (s), 1671 (s); δ_{s} (CH₃) 1385 (m); *v*(C–O) 1292 (s); Fc 1096 (m), 1070 (m), 1030 (m); PF₆⁻ 840 (s); PPh₂ 483 (composed m). HR LSIMS: *m*/*z* [C₃₈H₄₃O₃PClFeRu]⁺ ([M – PF₆]⁺) calcd 771.1041, found 771.103. For the instability of this compound at ambient conditions, no relevant microanalytical data could be obtained.

[(η⁶-C₆Me₆)Ru(=C(OCH₃)CH₂Ph)(Hdpf-*P*)(Cl)] (4c). 4 (374 mg, 0.50 mmol), NaPF₆ (86 mg, 0.51 mmol), and PhC=CH (0.15 mL, 1.4 mmol) gave 4c (424 mg, 86%) as a rusty-orange solid. ¹H NMR (C[²H]Cl₃): δ 1.77 (s, 18 H, C₆Me₆), 2.52 (d, ²J_{HH} = 13.3 Hz, 1 H, AB CH₂), 3.99 (s, 2 H, C₅H₄), 4.11 (s, 2 H, C₅H₄), 4.52 (s, 3 H, OMe), 4.66 (br s, 2 H, C₅H₄), 4.73 (s, 2 H, C₅H₄), 7.00-7.11 (m, 2 H, CH₂Ph), 7.21-7.30 (m, 3 H, CH₂Ph), 7.58-8.11 (br m, 10 H, PPh₂). ³¹P{¹H} NMR (C[²H]-Cl₃): δ -143.1 (sept, ¹J_{PF} = 712 Hz, PF₆⁻), 31.9 (s, Hdpf). IR (cm⁻¹): ν(CH) 3090 (w), 2920 (w); ν(C=O) 1716 (s), 1678 (s); δ_s(CH₃) 1386 (m); ν(C-O) 1263 (s), 1301 (s); Fc 1097 (m), 1037 (s), 1003 (m); PF₆⁻ 840 (s); PPh₂ 483 (composed s). Anal. Calcd for C₄₄H₄₇O₃F₆P₂ClFeRu: C, 53.27; H, 4.77; P, 6.24. Found: C, 52.88; H, 4.86; P, 6.24. HR LSIMS: m/z [C₄₄H₄₇O₃-PClFeRu]⁺ ([M - PF₆]⁺) calcd 847.1356, found 847.135.

Structure Determination. Thin, plate-like and fragile crystals of **4a**·CH₂Cl₂ were grown by gas-phase diffusion of pentane into a dichloromethane solution of **4a**. They were isolated by decantation and mounted on a glass fiber by epoxy cement. The diffractions were measured at 296(1) K on an Enraf-Nonius CAD 4-MACH III diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.710$ 73 Å) and $\theta - 2\theta$ scan. Intensities were collected at ψ -angles with the lowest absorption predicted. No further correction for absorption was made. The cell parameters were determined by least-squares from 25 centered diffractions with $12.0 \le \theta \le 12.8^{\circ}$.

The structure was solved by direct methods (SIR92³⁰), followed by consecutive Fourier syntheses and refined by fullmatrix least-squares on F^2 (SHELX93³¹). Non-hydrogen atoms were refined anisotropically, except those of the solvate dichloromethane. Aromatic (ferrocenyl, phenyl), methylene (FcC H_2 , CH_2Cl_2), and methyl (C_6Me_6 , OCH_3) hydrogens were fixed in theoretical positions to fit aromatic C–H (0.93 Å), ideal methylene group (C–H 0.97 Å), or electron density maxima (C–H 0.96 Å), respectively, with $U_{iso}(H) = 1.2 U_{eq}(C)$. The carboxylic hydrogen was identified on a difference electron density map and refined. The hexafluorophosphate anion and dichloromethane are partly disordered due to high symmetry or weak secondary bonding, respectively. The small crystal volume and the presence of partly disordered moieties are responsible for the higher values of the *R* indices.

Acknowledgment. This work was supported by the Grant Agency of Charles University, the Grant Agency of Czech Republic, and the CNRS. P.Š. gratefully acknowledges a fellowship in Rennes.

Supporting Information Available: Tables of crystallographic data, calculated and refined positional parameters, anisotropic thermal parameters, and intramolecular distances and angles and a packing diagram of **4a**·CH₂Cl₂ (14 pages). Ordering information is given on any current masthead page.

OM970478K

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