tion than that found in the 2,2′-bipyridine or 1,10-phenanthroline complexes.[26,28,33,34] The observation that the weaker base, 2,2′-bipyrimidine, exhibits a large dihedral angle of about 44° between the C_2B_3 face and the planar Lewis base is consistent with this trend.[27-29] However, the dihedral angle of 11.0° between the two ligands in IV suggests that the interactions between Ga and N-donor atoms are extremely strong and that the the apical Ga is severely slipped toward the unique boron despite the weaker basicity of the 2,2′-bipyrimidine ligand. This is precisely what has been found in the structure of IV. Perhaps, the greater Lewis acidity of the apical gallium is responsible for the unusually strong bonds that exist between the gallacarborane I and 2,2′-bipyrimidine in the donor–acceptor complex IV. As in the cases of the stannacarborane and plumbacarborane systems, the trans orientation of the gallacarboranes in IV is favored on steric grounds.[28,29]

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Supplementary Material Available: Listings of IR absorptions (Table S-1) and mass spectrometric data (Table S-2) for I–VI and tables of anisotropic displacement coefficients (Table S-3), torsion angles (Table S-4), and H-atom coordinates and isotropic displacement coefficients for I and IV (Table S-5) (10 pages); a listing of structure factors for I and IV (Table S-6) (16 pages). Ordering information is given on any current masthead page.

Synthesis and Reactivity of Neutral and Ionic π-Adducts of Functional Arenes. X-ray Crystal Structures of $\{[(C_5Me_5)Ru]_2(\eta^6,\eta^6\text{-}PhC{\equiv}CPh)\}(CF_3SO_3)_2$, $(C_5Me_5)Ru(\eta^6\text{-}PhCOO)$, and $[(C_5Me_5)(MeCN)Ru(\mu_2\text{-}\eta^2,\eta^4\text{-}C_4H_2Ph_2)Ru(C_5Me_5)](CF_3SO_3)$

Xiao Dong He, Bruno Chaudret,* Françoise Dahan, and Yong-Sheng Huang

Laboratoire de Chimie de Coordination du CNRS, UP No. 8241 liée par conventions
à l'Université Paul Sabatier et à l'Institut National Polytechnique, 205 route de Narbonne,
31077 Toulouse Cedex, France

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The protonation of $[Cp^*Ru(OMe)]_2$ (1) in the presence of functional arenes, viz. diphenylacetylene, stilbene, benzophenone, phenol, or benzoic acid, yields the π-arene adducts $[Cp^*Ru(\eta^6\text{-}PhC{\equiv}CPh)](CF_3SO_3)$ (5), $[(Cp^*Ru)_2(\eta^6,\eta^6\text{-}PhC{\equiv}CPh)](CF_3SO_3)_2$ (6), $[(Cp^*Ru)_2(\eta^6,\eta^6\text{-}PhCH{=}CHPh)](CF_3SO_3)_2$ (7), $[(Cp^*Ru)_2(\eta^6,\eta^6\text{-}PhCOPh)](CF_3SO_3)_2$ (9), $[Cp^*Ru(\eta^6\text{-}PhOH)](CF_3SO_3)$ (11), and $[Cp^*Ru(\eta^6\text{-}PhCOOH)](CF_3SO_3)$ (14). It is noteworthy that the monoadducts (5) and bis adducts (6) can be obtained with diphenylacetylene, whereas with stilbene and benzophenone the bis adducts (7 and 9) are preferentially obtained under the same conditions. This can be related both to the electron-releasing effect of the "Cp^*Ru^+" fragment and to the better transmission of electronic effects. 1 can be directly protonated by phenol and benzoic acid to yield $[Cp^*Ru(\eta^5\text{-}C_6H_5O)]$ (12) and $[Cp^*Ru(\eta^6\text{-}PhCOO)]$ (15). 15 shows a zwitterionic character ascertained by an X-ray crystal structure determination and its reactivity. 12 reacts with CH_3I to give $[Cp^*Ru(\eta^6\text{-}PhOCH_3)]^+$ (13), obtained independently from Cp^*Ru^+ and $PhOCH_3$ but not with a primary amine. Finally, the protonation of $[Cp^*Ru(OMe)]_2$ in the presence of benzonitrile or phenylacetylene leads to untractable mixtures containing both π-aromatic and σ-bonded (PhCN) or more complicated ($PhC{\equiv}CH$) derivatives. However, the reaction of $[Cp^*Ru(MeCN)_3](CF_3SO_3)$ (17) with phenylacetylene affords the paramagnetic complex $[Cp^*(MeCN)Ru(\mu_2\text{-}\eta^2,\eta^4\text{-}C_4H_2Ph_2)RuCp^*](CF_3SO_3)$ (18) in high yield. The structures of 6, 15, and 18 have been ascertained by X-ray crystal structure determination.

Introduction

Coordination to a transition metal has been shown to activate aromatic hydrocarbons toward nucleophilic substitution,[1,2] nucleophilic addition, etc.[1,3] Numerous organic syntheses have been carried out in this way for the last 20 years, mainly using the "$Cr(CO)_3$" fragment.[4] It has even been demonstrated lately that catalytic reactions could be assisted by this method.[5]

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However, the scope of applications of transition-metal arene compounds is not limited to synthetic use since such derivatives have been used recently both in bioorganometallic chemistry through hormone coordination[6] and in material science after coordination to arenes of specific shapes.[7]

Group 8 sandwich compounds of the type CpM(arene)$^+$ (Cp = C_5H_5, C_5Me_5) have been studied for a long time.[8] Astruc et al. have particularly developed the electron-transfer reactions involving these species.[9]

The first such ruthenium derivative [CpRu(C_6H_6)]Cl has been prepared as early as 1973.[10] More recently, the CpRu$^+$ fragment obtained from [CpRu(MeCN)$_3$]$^+$ has been employed by different authors to coordinate either to molecules of biological importance[11] or to sulfur heterocycles for studying hydrodesulfurization (HDS) models.[12] Mann et al. have found an entry into a similar chemistry involving the pentamethylcyclopentadienyl ligand (Cp*) but using a nongeneral method.[13] In the last few years, after the discovery of a simple synthesis of [Cp*RuCl$_2$]$_n$,[14] three groups including ours have found new easy accesses to such [Cp*Ru(arene)]$^+$ derivatives. Fagan et al. used the cation [Cp*Ru(MeCN)$_3$](CF_3SO_3) obtained by reduction of [Cp*RuCl$_2$]$_2$ with LiBHEt$_3$ followed by chlorine abstraction by CF_3SO_3Ag.[7b] Koelle et al. described the protonation of the dinuclear methoxy derivative [Cp*Ru(OMe)]$_2$ by NH_4^+ in the presence of arenes,[15] whereas we independently found two accesses to the "Cp*Ru$^+$" fragment either produced free of solvent by protonation of [Cp*Ru(OMe)]$_2$ by CF_3SO_3H in the presence of arenes[16] or by zinc reduction of [Cp*RuCl$_2$]$_n$ in a weakly coordinating solvent (CH_2Cl_2, THF, MeOH, ...).[17]

The Cp*Ru$^+$ fragment was shown to have a strong affinity for arenes, even in the presence of a good σ-donor ligand such as acetonitrile.[7] We found that unusual π-complexes such as π-pyridine, π-3,5-lutidine, or π-4-picoline could be obtained by either method but that an electronic rather than steric stabilization of the π-complex was observed and that the reactions were very sensitive to the nature of the solvent.[17] Typically, a very polar solvent, e.g., methanol, acetone, or acetonitrile, led to σ- rather than π-adducts. In other words, it was possible to orientate the reaction to obtain the expected coordination of these bifunctional molecules.

Table I. ^{1}H NMR Data for Complexes 5–16 in $(CD_3)_2CO$ at 200.133 MHz

compd	Cp*	coordinated arene	others
5	2.18 s, 15 H	6.35 m, 5 H	7.77 m, 2 H_m, 7.61 m, 3 $H_{o,p}$ (η^6-PhC≡C*Ph*)
6	2.20 s, 30 H	6.53 m, 4 H_m, 6.38 m, 6 $H_{o,p}$	
7	2.12 s, 30 H	6.47 m, 4 H_o, 6.31 m, 6 $H_{,m,p}$	7.38 s, 2 H (PhC*H*=C*H*Ph)
8	2.07 s, 15 H	6.54 m, 2 H_o, 6.16 m, 3 $H_{m,p}$	7.51 m, 5 H (η^6-PhCH=CH*Ph*)
9	2.11 s, 30 H	6.84 m, 4 H_o, 6.49 m, 6 $H_{m,p}$	
10	2.20 s, 15 H	6.90 m, 2 H_o, 6.60 m, 3 $H_{m,p}$	8.10 m and 7.75 m, 5 H (η^6-PhCO*Ph*)
11	2.16 s, 15 H	6.02 m, 4 $H_{m,o}$, 5.80 m, 1 H_p	
12	2.00 s, 15 H	5.46 dd,[a] 2 H_m, 5.27 t,[b] 1 H_p, 4.96 d,[c] 2 H_o	7.26 m, 2 H*m*, 6.98 m, 2 H_o, 6.86 m, 1 H_p (*Ph*OH)
13[d]	2.01 s, 15 H	5.92 m, 4 $H_{m,o}$, 5.66 m, 1 H_p	3.81 s, 3 H (PhOCH_3)
14	2.13 s, 15 H	6.62 m, 2 H_m, 6.29 m, 3 $H_{o,p}$	
15	2.07 s, 15 H	6.50 m, 2 H_m, 6.02 m, 3 $H_{o,p}$	
16	2.11 s, 15 H	6.70 m, 2 H_m, 6.47 m, 3 $H_{o,p}$	4.14 s, 3 H (PhCO_2CH_3)

[a] $J_{HH'}$ = 5.3 Hz, $J_{HH''}$ = 6.5 Hz. [b] $J_{HH'}$ = 5.3 Hz. [c] $J_{HH'}$ = 6.5 Hz. [d] In CD_2Cl_2.

If one wants to employ metal arene complexes in material science, biology, or even organic synthesis, this involves coordination of a metal fragment to polyfunctional and possibly polycyclic molecules. To our knowledge, no systematic study of the coordination of ruthenium metal fragment to such molecules has been published so far. However, examples of such compounds are already known: coordination of ruthenium to molecules of biological importance by Moriarty,[11] to heterocycles by Angelici[12] and Fish,[18] to styrene by Fagan et al.,[7] to phenolate by Tilley,[19] and to polyaromatics by Koelle.[20] In the case of CpFe$^+$ analogues, many such complexes have been known for a long time.[21]

We report in this paper the reactivity of the Cp*Ru$^+$ fragment generated by protonation of [Cp*Ru(OMe)]$_2$ toward arenes containing a function very likely to coordinate to a transition metal, i.e., acetylenes, olefin, carboxylic acid, ketone, phenol, and nitrile. As indicated above, after the work of Fagan, we already know that styrene gave η^6-adducts with Cp*Ru$^+$. We also report the crystal structures of three products resulting from these reactions. A preliminary account of a part of this work has been published.[16]

Results and Discussion

Stoichiometric protonation by CF_3SO_3H of the dimer [Cp*Ru(OMe)]$_2$ (1) prepared by the method of Koelle and Kossakowski[22] in the presence of an arene in a polar sol-

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Table II. ^{13}C NMR Data for Selected Complexes in $(CD_3)_2CO$

	δ			
compd	C_5Me_5	C_5Me_5 (J_{CH})[f]	coordinated arene (J_{CH})	others[e] (J_{CH})
5[a]	97.63 s	8.24 q (129)	89.87 d (184), 87.89 d (183), 87.80 d (183), 83.37 s	132.34 d (152)*, 130.24 d (162)*, 129.17 d (147)*, 121.31 s*, 85.35 s, $C\equiv C'$, 91.41 s, $C\equiv C'$, 85.62 s, $C\equiv C$
6[a]	98.05 s	9.71 q (119)	90.13 d (180), 88.11 d (180), 85.86 d (180), 83.16 s	
9[b]	98.60 s	9.66 q (128)	94.37 s, 90.00 d (179), 88.30 d (171), 87.95 (178)	192.7 s, CO
11[b]	95.69 s	9.77 q (129)	130.67 s, 86.44 d (178), 84.45 d (178), 77.44 d (175)	
12[a]	91.77 s	9.96 q (129)	149.04 s, 86.66 d (170), 78.80 d (174), 78.12 d (167)	158.71 s**, 129.38 d (160)**, 118.57 d (143)**, 115.67 d (158)**
14[c]	95.79 s	9.54 q	88.67 87.49 87.22	
15[d]	97.74 s	9.55 q	89.15 88.61 87.91	

[a] At 50.324 MHz. [b] At 61.896 MHz. [c] At 61.896 MHz, {^{1}H}BB. [d] At 50.324 MHz {^{1}H}BB. [e] * noncoordinated arene, ** free phenol. [f] All J values in Hz.

vent (THF, acetone, or, best, CH_2Cl_2) affords the sandwich complex [Cp*Ru(arene)](CF_3SO_3). The yield depends on the arene, but as a test, we first performed the reaction in the presence of benzene, toluene, and thiophene and obtained [Cp*Ru(arene)](CF_3SO_3) as a crystallized material in ~90% (2) (in the presence of excess benzene), 60% (3), and 80% (4) yield, respectively (1:1 reactions). The latter values demonstrate the advantage of this method compared to the one involving zinc reduction of $[Cp^*RuCl_2]_n$ in polar solvents.[17] These encouraging results prompted us to study the selectivity of the η^6-coordination of arenes in bifunctional molecules such as acetylenes, benzophenone, phenols, carboxylic acid, and nitriles.

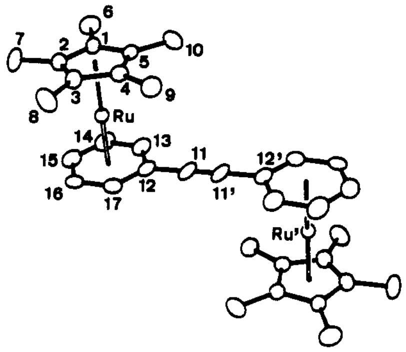

Figure 1. ORTEP view of the dication $[(Cp^*Ru)_2(\eta^6,\eta^6\text{-}PhC\equiv CPh)]^{2+}$ (6).

Table III. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for $[(C_5Me_5Ru)_2(PhCCPh)](CF_3SO_3)_2$ (6)[a]

Ru–M(1)	1.801 (4)	Ru–M(2)	1.692 (4)
M(1)–Ru–M(2)	179.2 (2)	Ru–C(1)	2.172 (3)
Ru–C(2)	2.166 (4)	Ru–C(3)	2.177 (4)
Ru–C(4)	2.174 (3)	Ru–C(5)	2.169 (3)
Ru–C(12)	2.195 (4)	Ru–C(13)	2.180 (4)
Ru–C(14)	2.201 (4)	Ru–C(15)	2.193 (4)
Ru–C(16)	2.212 (4)	Ru–C(17)	2.192 (4)
C(1)–C(2)	1.408 (5)	C(1)–C(6)	1.495 (5)
C(2)–C(3)	1.421 (6)	C(2)–C(7)	1.511 (6)
C(3)–C(4)	1.428 (5)	C(3)–C(8)	1.499 (6)
C(4)–C(5)	1.434 (5)	C(4)–C(9)	1.496 (5)
C(5)–C(1)	1.438 (5)	C(5)–C(10)	1.503 (6)
C(11)–C(12)	1.451 (6)	C(11)–C(11)^i	1.147 (9)
C(12)–C(13)	1.415 (6)	C(15)–C(16)	1.416 (8)
C(13)–C(14)	1.414 (7)	C(16)–C(17)	1.390 (7)
C(14)–C(15)	1.388 (9)	C(17)–C(12)	1.370 (7)
C(12)–C(11)–C(11)^i	177.6 (7)	C(11)–C(12)–C(17)	121.5 (4)
C(17)–C(12)–C(13)	118.5 (4)	C(11)–C(12)–C(13)	119.9 (4)

[a] M(1) and M(2) are the centroids of pentamethylcyclopentadienyl and phenyl rings, respectively. i is the symmetry operation $-x$, $1 - y$, $1 - z$.

Acetylenes. With diphenylacetylene, two complexes may be obtained from the reaction, either a 1:1 adduct or a 1:2 adduct. We have found that the two complexes can be selectively prepared according to the stoichiometry of the reaction. Thus, protonation of $[Cp^*Ru(OMe)]_2$ in the presence of 2 equiv of diphenylacetylene in CH_2Cl_2 yields white crystalline $[Cp^*Ru(\eta^6\text{-}PhC\equiv CPh)](CF_3SO_3)$ (5), whereas in the presence of only 1 equiv of diphenylacetylene the reaction leads to $[(Cp^*Ru)_2(\eta^6,\eta^6\text{-}PhC\equiv CPh)](CF_3SO_3)_2$ (6), which is similarly white and crystalline. Both compounds are thermally stable and air-stable. 5 shows a $\nu_{C\equiv C}$ stretch at 2227 cm^{-1} as expected for an unsymmetrical acetylene, whereas no infrared active band is observed in this region in the case of 6. The ^{1}H NMR spectrum of 6 shows a shift to high field of the phenyl protons of about 1 ppm characteristic of π-coordination to the Cp^*Ru^+ fragment. Similarly, the ^{13}C NMR spectrum shows a shift of ca. 30 ppm to high field for the phenyl carbons but only ca. 4 ppm for the acetylene ones (the chemical shifts of the acetylenic carbons of free diphenylacetylene are observed at δ 89.4 ppm). The NMR spectra of 5 clearly show the free and coordinated phenyl rings in a 1:1 ratio (Tables I and II). Interestingly, the chemical shift of the acetylenic carbon adjacent to the free phenyl ring in 5 is observed in the region expected for a free acetylene. The structure of 6 has been ascertained by X-ray diffraction (Figure 1 and Table III). The structure consists of two Cp*Ru units centrosymmetrically bonded to a diphenylacetylene molecule in an η^6-mode. The bonding is essentially similar to the structure of other $[Cp^*Ru(\eta^6\text{-arene})]^+$ derivatives, many examples of which have been recently described by Fagan et al.[7] The average C–C(ring) and C–Me distances of the Cp* ligand are 1.426 (5) and 1.501 (6) Å, respectively. The distance of the centroid of the Cp* ligand to ruthenium is 1.801 (4) Å, as observed for Fagan's complexes. The phenyl groups of diphenylacetylene are symmetrically bonded to ruthenium with an average C–C distance of 1.399 (7) Å and a Ru–centroid distance of 1.692 (4) Å. The most interesting feature of this structure is the C≡C distance (1.147 (9) Å), which seems quite unaffected by ruthenium coordination. This is to be correlated with the observation of selective syntheses of the monoruthenium and bis-ruthenium derivatives of diphenylacetylene, which indicates that after the first coordination of ruthenium the remaining phenyl ring is neither activated nor significantly deactivated. This can be related to the poor electron transmission in acetylenic systems.

Phenylacetylene. Although a chromium compound containing η^6-bonded phenylacetylene has been reported to be prepared by indirect systhesis,[23] the direct coordination of a metal fragment to the phenyl ring of phenylacetylene represents a challenge since two other reactive functions are present in the molecule. The reaction of $[Cp^*Ru(OMe)]_2$ with CF_3SO_3H in the presence of phenylacetylene yields a solution shown to contain a complicated mixture of products including some η^6-bonded phenylacetylene derivatives as minor components. Attempts to separate or crystallize the components of this mixture were unsuccessful. However, when carrying out the reaction starting from $[Cp^*Ru(MeCN)_3]CF_3SO_3$, we obtained a green paramagnetic crystalline material shown by X-ray crystallography to be a monocationic dimer (vide infra).

***trans*-Stilbene.** Although it has previously been shown that the Cp^*Ru^+ fragment could coordinate more easily to the phenyl ring of styrene than to the double bond, we performed the same reaction with stilbene. Like for diphenylacetylene, a white air-stable product could be obtained in a microcrystalline form. However, when employing a stilbene:Ru ratio of 1:1, the major product (~ 85% based on Ru) was the 2:1 adduct $[(Cp^*Ru)_2(\eta^6,\eta^6\text{-}PhC_2H_2Ph)](PF_6)_2$ (**7**). The NMR spectrum of **7** shows the phenyl protons at δ 6.47 (2 H, ortho) and 6.30 ppm (3 H, meta, para) and the olefinic proton at δ 7.38 ppm. An NMR spectrum of the remaining solution shows the presence of another complex on the basis of which we propose the structure $[Cp^*Ru(\eta^6\text{-}PhCHCHPh)](CF_3SO_3)$ (**8**). **8** could not be obtained selectively like **5** by adding dropwise a solution of Cp^*Ru^+ prepared by reaction of $[Cp^*Ru(OMe)]_2$ with CF_3SO_3H in CH_2Cl_2 on a solution of stilbene in CH_2Cl_2 in a 1:1 ratio, but rather a mixture of **7** and **8** was again obtained.

The preferred formation of **7** when protonating a 1:1 mixture of **1** presumably reflects an electronic activation of the second phenyl ring after the first coordination of ruthenium. This result seems surprising since it would mean an electron-releasing effect of the Cp^*Ru^+ fragment, which is unexpected.

Benzophenone. In order to give more evidence for the effects described here above, we performed the 1:1 reaction between benzophenone and Cp^*Ru^+. In that case, the only isolable product was the pale yellow air-stable crystalline bis-ruthenium adduct, $[(Cp^*Ru)_2(\eta^6,\eta^6\text{-}PhCOPh)](CF_3SO_3)_2$ (**9**). From NMR spectra, we could deduce the presence of a very small amount (<10%) of the 1:1 adduct $[Cp^*Ru(\eta^6\text{-}PhCOPh)](CF_3SO_3)$ (**10**). The NMR spectrum of **9** shows the phenyl protons at δ 6.84 (2 H, ortho) and 6.49 ppm (3 H, meta and para).

This reaction demonstrates that, like for stilbene and perhaps more efficiently, the coordination of one phenyl ring activates the other phenyl ring toward coordination through electronic effects.

Phenol. π-Bonded phenoxide derivatives of ruthenium have been described several years ago by Wilkinson et al.,[24] while Tilley et al.[19] recently reported the reaction of 2,6-di-*tert*-butylphenoxide with $[Cp^*RuCl]_4$ leading to the η^5-phenoxide adduct. However, in this case, no simple reaction with phenol was performed.

Table IV. ^1H NMR Data for the π-Complexed Ring of Various Mixtures of 11 and 12

11/12	solvent	δ H	δ H_m	δ H_o
1/0	$(CD_3)_2CO$	5.27 (t)	5.46 (dd)	4.96 (d)
2/1	CD_2Cl_2	5.11 (t)	5.30 (t)	5.20 (d)
1/1	CD_2Cl_2	5.18 (t)	5.35 (m)	5.35 (m)
1/2	CD_2Cl_2	5.26 (t)	5.43 (m)	5.43 (m)
0/1	$(CD_3)CO$	5.88 (m)	6.02 (m)	6.02 (m)

The reaction of $[Cp^*Ru(OMe)]_2$ with CF_3SO_3H in the presence of phenol yields $[Cp^*Ru(\eta^6\text{-}PhOH)](CF_3SO_3)$ (**11**) as a white crystalline material. **11** was characterized by ^1H and ^{13}C NMR, and more specifically, the phenyl protons of the phenol ring are observed at δ 5.88 ppm (1 H, para) and 6.02 ppm (4 H, meta, ortho). The phenyl carbons were found near 80 ppm as expected, except for the one bearing the OH group, which resonates at δ 130.67 ppm. This reaction is not unexpected, but more surprisingly, we found that the weak acid phenol was itself able to react with $[Cp^*Ru(OMe)]_2$ to give the neutral η^5-phenoxide $[Cp^*Ru(\eta^5\text{-}C_6H_5O)]\cdot 2PhOH$ (**12**). However, π-phenoxo derivatives have been obtained by direct attack of excess phenol on $RuH_2(PPh_3)_4$.[24] The chemical shift of the ring protons of **11** are shifted ca. 1 ppm to high field as expected, whereas those of **12** are found ca. 1 ppm at further higher field. Interestingly, the values we found, viz. δ 4.96 (2 H, ortho), 5.27 (1 H, para), and 5.46 ppm (2 H, meta), are nearly identical with those found for $RuH(OPh)(PPh_3)_2\cdot 2PhOH$ (δ 4.95, 5.35, and 5.45 ppm). The shift to high field of the ortho hydrogens is presumably indicative of some loss of aromaticity of the molecule. It is well-known that these π-phenoxide molecules are not flat but bent.[19,24] Similar iron complexes are known.[21c]

We were interested to see whether the interconversion between **11** and **12** was an easy process. As expected, protonation of **12** with CF_3SO_3H gave **11**, whereas deprotonation of **11** with NEt_3 yielded back **12**. Nevertheless, no exchange with free phenol was observed, but a 1:1 mixture of **11** and **12** only gave a mean signal at all temperatures. Since this behavior could be attributed to the existence of a defined hydrogen-bonded dimer, $\{Cp^*RuPhO\cdots HOPhRuCp^*\}^+$, we performed the same reaction varying the relative concentration of **11** and **12**. Table IV shows the variation of the position of the phenoxo protons as a function of the relative concentration of **11** and **12**. The shift to high field of the ortho protons is particularly clear.

This result proves the ease of deformation of the phenoxo cycle. Since this process is rapid even at −80 °C as detected by ^1H NMR, the activation barrier is less than ca. 6 kcal/mol.

Another description of the structure of **12** in solution would be a zwitterionic complex containing an aromatic π-phenoxide ligand (Scheme I), thus bearing a negative charge on the oxygen atom. The strong hydrogen bonding of these π-phenoxo complexes with free phenol observed by NMR techniques and microanalysis (see Tables I and II and Experimental section) is in agreement with this proposal. Such a zwitterionic π-benzoate adduct is described below. In order to check this hypothesis, **12** was reacted with CH_3I and $i\text{-}PrNH_2$. In the case of a negative charge, the first reaction was expected to yield $[Cp^*Ru(\eta^6\text{-}PhOCH_3)]^+$ through nucleophilic substitution, while in the case of a strong C=O double-bond character, the second reaction should have yielded an imine. The first reaction is rapid and yields the expected $[Cp^*Ru(\eta^6\text{-}PhOCH_3)]^+$ (**13**) prepared independently from $[Cp^*Ru(OMe)]_2$, CF_3SO_3H, and anisole, whereas the second reaction does not work. Although this is not a definitive

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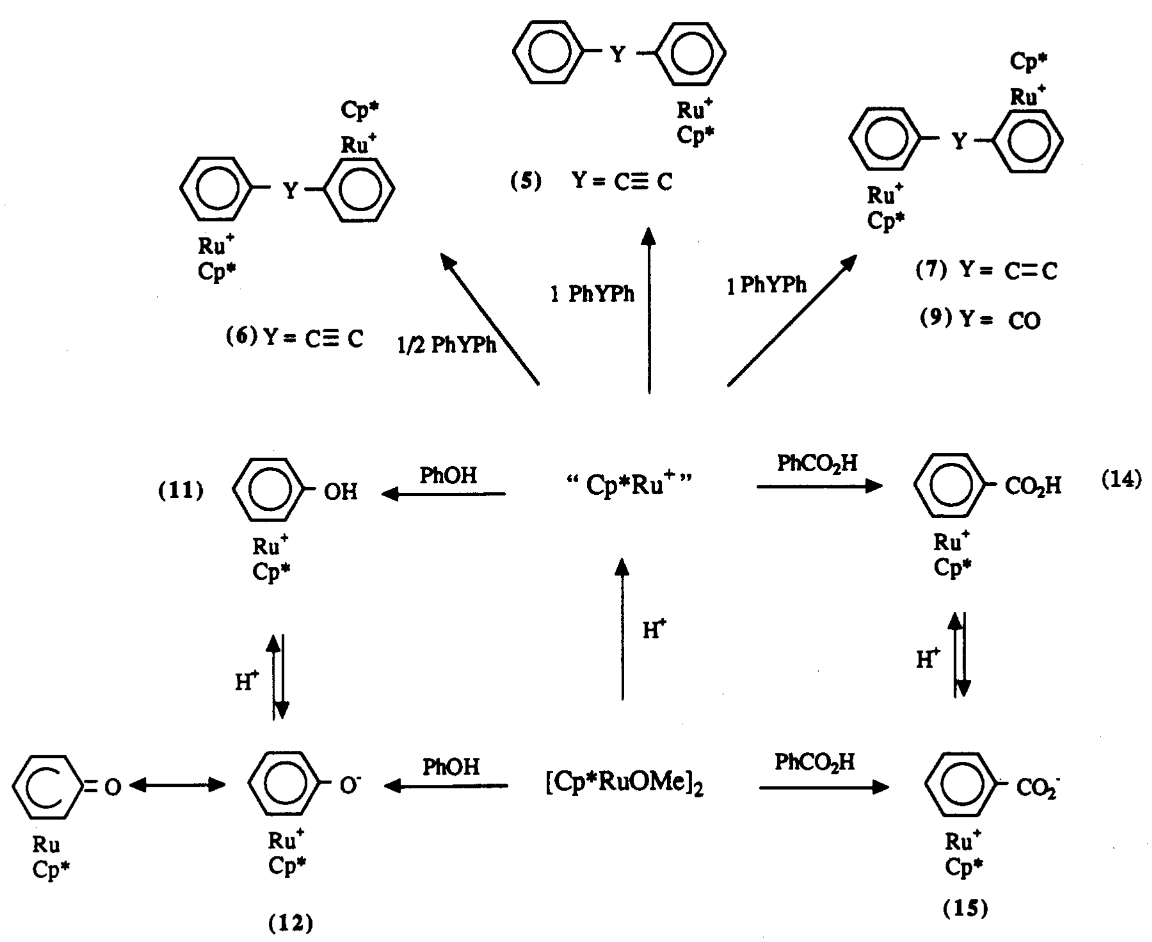
[23] Knox, G. R.; Leppard, D. G.; Pauson, P. L.; Watts, W. E. *J. Organomet. Chem.* **1972**, *34*, 347.

[24] Cole-Hamilton, D. J.; Young, R. J.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 1995.

Scheme I. Reactions of the "Cp*Ru$^+$" Fragment with Various Arenes



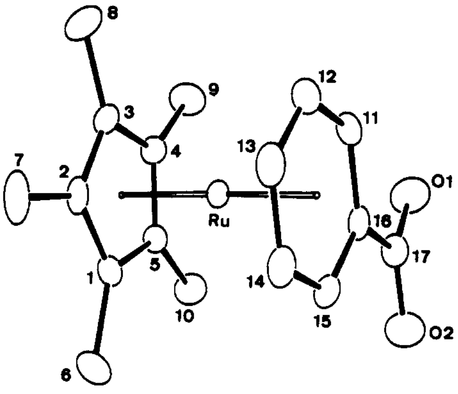


Figure 2. ORTEP view of Cp*Ru(η^6-PhCOO) (15).

Table V. Selected Bond Lengths (Å) and Angles (deg) with Standard Deviations in Parentheses for 0.7[(C_5Me_5)Ru(PhCOO)]$_2H_2O$ • 0.3[(C_5Me_5)Ru(PhCOOCH$_3$)]OH (15′)^a

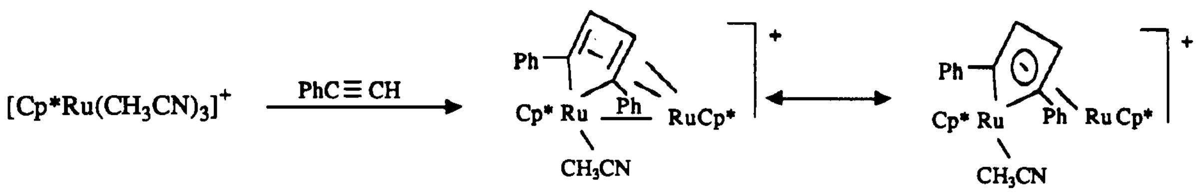
Ru–M(1)	1.811 (4)	Ru–(2)	1.707 (4)
Ru–C(1)	2.174 (4)	Ru–C(11)	2.217 (4)
Ru–C(2)	2.159 (4)	Ru–C(12)	2.210 (4)
Ru–C(3)	2.188 (4)	Ru–C(13)	2.212 (4)
Ru–C(4)	2.190 (4)	Ru–C(14)	2.209 (4)
Ru–C(5)	2.186 (4)	Ru–C(15)	2.215 (4)
M(1)–Ru–M(2)	178.5 (2)	Ru–C(16)	2.229 (4)
C(1)–C(2)	1.424 (6)	C(1)–C(6)	1.499 (6)
C(2)–C(3)	1.426 (6)	C(2)–C(7)	1.507 (6)
C(3)–C(4)	1.423 (5)	C(3)–C(8)	1.500 (7)
C(4)–C(5)	1.427 (6)	C(4)–C(9)	1.493 (6)
C(5)–C(1)	1.431 (5)	C(5)–C(10)	1.500 (6)
C(11)–C(12)	1.416 (6)	C(16)–C(11)	1.420 (6)
C(12)–C(13)	1.407 (6)	C(1)–C(17)	1.513 (6)
C(13)–C(14)	1.405 (7)	C(17)–O(1)	1.237 (6)
C(14)–C(15)	1.414 (6)	C(17)–O(2)	1.257 (6)
C(15)–C(16)	1.410 (6)	Ru–C(16)–C(15)	70.9 (2)
C(15)–C(16)–C(11)	119.0 (4)	Ru–C(16)–C(11)	70.9 (2)
C(11)–C(16)–C(17)	121.0 (4)	Ru–C(16)–C(17)	127.2 (3)
C(15)–C(16)–C(17)	119.9 (4)	C(16)–C(17)–O(2)	115.9 (4)
C(16)–C(17)–O(1)	118.0 (4)	O(1)–C(17)–O(2)	126.1 (4)
Water Molecules, Hydrogen Bonds, and Disordered Methyl			
Ow(1)–H1(w1)	0.97 (4)	Ow(1)–H2(w1)	0.97 (4)
Ow(1)...O(1)^i	2.788 (6)	Ow(1)...O(2)	2.832 (6)
H1(w1)...O(1)^i	1.87 (3)	H2(w1)...O(2)	1.88 (4)
Ow(1)–H1(w1)–O(1)^i	156 (4)	Ow(1)–H2(w1)...O(2)	167 (4)
Ow(2)...O(2)	2.624 (6)	Ow(2)...C(18)	1.10 (1)
O(2)–C(18)	1.540 (9)	C(17)–O(2)–C(18)	116.9 (6)
H1(w1)–Ow(1)–H2(w1)	109 (4)		

^{a} M(1) and M(2) are, respectively, the centroids of cyclopentadienyl and phenyl rings i is the symmetry operation $^1/_2 - x$, $^1/_2 + y$, $^1/_2 - z$.

demonstration, these reactions show that a significant negative charge is present on the oxygen. Thus, the fast exchange 11 and12 is presumably not a true dearomatization process.

Benzoic Acid. 1 reacts rapidly with benzoic acid after protonation with CF_3SO_3 to yield the η^6-adduct [Cp*Ru(η^6-PhCOOH)](CF_3SO_3) (14). However, the direct reaction of 1 with benzoic acid produces the neutral complex Cp*Ru(η^6-PhCOO) (15). Like 11 and 12, 14 and 15 are interconvertible by protonation and deprotonation. The IR spectrum of 14 shows a ν_{CO} band at 1720 cm^{-1} and ν_{OH} one at 3085 cm^{-1} as expected for a hydrogen-bonded carboxylic acid. The structure of 14 is thus presumably dimeric. The infrared spectrum of 15 shows in contrast a single ν_{CO} band at 1600 cm^{-1} as expected for a carboxylato derivative. The ^{1}H NMR spectra show a small (ca. 0.1, 0.2 ppm, see Table I) shift to high field of the phenyl protons of 15 compared to those of 14. This reflects the higher electron density on the phenyl ring of 15 but no dramatic change and no deformation of the cycle. The ^{13}C NMR spectra are similar.

Scheme II. Reactions of the "Cp*Ru⁺" Fragment with Diphenylacetylene



(18)

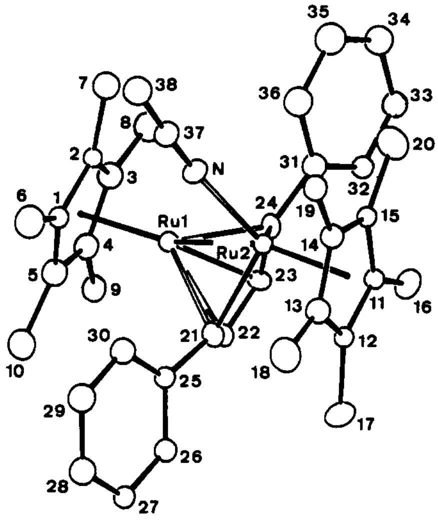


Figure 3. ORTEP view of the cation $[Cp^*(MeCN)Ru(\mu_2\text{-}\eta^2,\eta^4\text{-}C_4H_2Ph_2)RuCp^*]^+$ (18).

Table VI. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for $[(C_5Me_5)(MeCN)Ru(C_4H_2Ph_2)Ru(C_5Me_5)]CF_3SO_3$ (18)[a]

Ru(1)–Cp(1)	1.922 (5)	Ru(2)–Cp(2)	1.957 (5)
Ru(1)–C(1)	2.247 (5)	Ru(2)–C(11)	2.263 (5)
Ru(1)–C(2)	2.181 (5)	Ru(2)–C(12)	2.413 (5)
Ru(1)–C(3)	2.238 (5)	Ru(2)–C(13)	2.404 (5)
Ru(1)–C(4)	2.366 (5)	Ru(2)–C(14)	2.247 (5)
Ru(1)–C(5)	2342 (5)	Ru(2)–C(15)	2.155 (5)
Ru(1)–C(21)	2.195 (8)	Ru(2)–C(21)	2.160 (7)
Ru(1)–C(22)	2.091 (7)	Ru(2)–C(24)	2.083 (7)
Ru(1)–C(23)	2.118 (7)	Ru(2)–N	2.089 (6)
Ru(1)–C(24)	2.003 (7)	Ru(1)–Ru(2)	2.6609 (8)
Cp(1)–Ru(1)–C(21)	137.4 (2)	C(21)–Ru(1)–C(22)	36.0 (3)
Cp(1)–Ru(1)–C(22)	130.1 (3)	C(21)–Ru(1)–C(23)	65.4 (3)
Cp(1)–Ru(1)–C(23)	134.3 (3)	C(21)–Ru(1)–C(24)	75.3 (3)
Cp(1)–Ru(1)–C(24)	145.7 (2)	C(21)–Ru(1)–Ru(2)	51.7 (2)
Cp(1)–Ru(1)–Ru(2)	150.8 (1)	C(22)–Ru(1)–C(23)	38.0 (3)
Cp(2)–Ru(2)–C(21)	109.2 (2)	C(22)–Ru(1)–C(24)	66.5 (3)
Cp(2)–Ru(2)–C(24)	116.0 (2)	C(22)–Ru(1)–Ru(2)	74.8 (2)
C(23)–Ru(1)–C(24)	36.6 (3)	C(23)–Ru(1)–Ru(2)	74.2 (2)
C(24)–Ru(1)–Ru(2)	50.7 (2)	C(21)–Ru(2)–C(24)	74.5 (3)
Cp*(2)–Ru(2)–N	123.6 (2)	C(21)–Ru(2)–N	113.9 (3)
Cp*(2)–Ru(2)–Ru(1)	155.8 (1)	C(24)–Ru(2)–N	109.4 (3)
C(24)–Ru(2)–Ru(1)	48.1 (2)	C(21)–Ru(2)–Ru(1)	52.9 (2)
C(22)–C(21)–C(25)	128.6 (7)	C(22)–C(23)–C(24)	114.3 (7)
Ru(1)–C(21)–C(22)	67.7 (4)	Ru(1)–C(23)–C(22)	69.9 (4)
Ru(1)–C(21)–C(25)	115.1 (5)	Ru(1)–C(23)–C(24)	66.9 (4)
Ru(2)–C(21)–C(22)	111.6 (5)	C(23)–C(24)–C(31)	120.9 (6)
Ru(2)–C(21)–C(25)	118.7 (5)	Ru(1)–C(24)–C(23)	76.5 (5)
Ru(1)–C(21)–Ru(2)	75.3 (2)	Ru(1)–C(24)–C(31)	133.4 (5)
C(21)–C(22)–C(23)	119.4 (7)	Ru(2)–C(24)–C(23)	117.1 (5)
Ru(1)–C(22)–C(21)	76.2 (5)	Ru(2)–C(24)–C(31)	117.2 (4)
Ru(1)–C(22)–C(23)	72.0 (4)	Ru(1)–C(24)–Ru(2)	81.2 (2)
N–C(37)	1.195 (11)	N–Ru(2)–Ru(1)	80.6 (2)
Ru(2)–N–C(37)	161.9 (6)	N–C(37)–C(38)	173.1 (9)
C(1)–C(6)	1.497 (12)	C(11)–C(16)	1.482 (11)
C(2)–C(7)	1.520 (11)	C(12)–C(17)	1.521 (10)
C(3)–C(8)	1.510 (10)	C(13)–C(18)	1.509 (12)
C(4)–C(9)	1.494 (10)	C(14)–C(19)	1.501 (10)
C(5)–C(10)	1.496 (10)	C(15)–C(20)	1.505 (11)
C(21)–C(22)	1.329 (11)	C(22)–C(23)	1.372 (10)
C(23)–C(24)	1.300 (10)	C(21)–C(25)	1.446 (9)
C(24)–C(31)	1.470 (8)	C(37)–C(38)	1.475 (13)

[a] Cp(1) and Cp(2) are the centroids of C(1), C(2), C(3), C(4), C(5) and C(11), C(12), C(13), C(14), C(15) cyclopentadienyl rings.

Since a zwitterionic structure is unusual although not unknown in organometallic chemistry,[21,25] a crystal structure determination was undertaken. The results are shown in Figure 2 and Table V. However, a disorder is present in the structure hereafter referred as 15′, which was shown to contain $0.7[Cp^*Ru(PhCOO)]\cdot 2H_2O$ and $0.3[Cp^*Ru(PhCOOCH_3)]OH$.

The structure consists of one Cp*Ru unit linked symmetrically to the six carbon atoms of the benzoate group. All the C–C distances within the Cp* ligand or the phenyl ring are found as expected for such compounds. The C(16)–C(17) distance (1.513 (6) Å) is also in the range admitted for a single C–C bond. The two C–O bonds (C(17)–O(1) = 1.237 (6) Å, C(17)–O(2) = 1.257 (6) Å) are short and similar, which demonstrates the zwitterionic character of complex 15. The other complex present, 15′, appears to be a π-methyl benzoate derivative, which would result from the esterification of the benzoato fragment (see Experimental Section). In order to confirm this hypothesis, 15 was reacted with CH_3OH and CH_3I. Both reactions led to the desired π-methyl benzoate compound but in low to moderate yield, respectively. The structure of the reaction products was assigned by comparison with an authentic sample of $[Cp^*Ru(\eta^6\text{-}PhCOOCH_3)](CF_3SO_3)$ (16) obtained independently from $[Cp^*Ru(OMe)]_2$, CF_3SO_3H, and $PhCOOCH_3$.

Benzonitrile. As in the case of phenylacetylene, the protonation of 1 by CF_3SO_3H in the presence of benzonitrile does not lead to a simple species but to complicated mixtures containing minor amounts of π-benzonitrile compounds, some σ-benzonitrile derivatives, and even some complexes without the Cp* ligand, as indicated by NMR spectroscopy. A precedent for this type of behavior has been observed in the case of the reaction of $[Cp^*RuCl]_4$ or Cp^*Ru^+ with pyridine. This reaction was not further investigated.

Reaction of $[Cp^*Ru(CH_3CN)_3](CF_3SO_3)$ with Phenylacetylene. In order to obtain a slower reaction with phenylacetylene and a better chance to get a π-adduct, we used as the starting material the tris-solvent adduct $[Cp^*Ru(CH_3CN)_3](CF_3SO_3)$ (17).

The reaction of 17 with 2 equiv of phenylacetylene in THF leads to a green precipitate analyzing for $[Ru_2(Cp^*)_2(PhC_2H)_2(MeCN)](CF_3SO_3)$ (18) (Scheme II). The complex is paramagnetic and its IR spectrum does not show any $\nu_{C\equiv C}$ band. However, the molecular structure of this compound was determined by X-ray crystallography and is shown in Figure 3 (see Table VI). It consists of dimeric units showing a short Ru–Ru distance (2.6609 (8) Å) corresponding to a single metal-metal bond. Ru(2) adopts a piano-stool environment composed of a Cp* lig-

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(25) Stebler-Röthlisberger, M.; Salzer, A.; Bürgi, H. B.; Ludi, A. *Organometallics* **1986**, *5*, 298.

and, one acetronitrile molecule, and two σ-bonded carbon atoms at the end of a C_4 fragment ((Ru(2)–C(24) = 2.083 (7) Å, Ru(2)–C(21) = 2.160 (7) Å). The other ruthenium atom (Ru(1)) is linked to a Cp* ligand, to Ru(2), and to the four carbon atoms of the C_4 fragment. It is interesting to compare the structural features of **18** with those of similar compounds. Thus, Singleton has reported the structure of CpRuBr($C_4H_2Ph_2$), which shows a substantial carbene character for the Ru–C bonds of the C_4 fragment (Ru–C = 1.942 (6) Å).[26] This is obviously not the case in **18**, the Ru–C bond lengths lying in the range admitted for such ruthenacyclopentadiene derivatives. Tilley et al. have recently prepared a similar but diamagnetic compound, Cp*Cl_2Ru(μ_2-η^2,η^4-C_4H_4)RuCp*.[27] The Ru–C distances of the ruthenacyclopentadiene ring are comparable in that case, but the C–C distances are clearly shorter in our case (1.30 (1)–1.37 (1) instead of 1.40–1.42 Å). Furthermore, Ru(1) lies only 0.3859 (6) Å out of the C_4 plane (maximum deviation for the carbon atoms: 0.046 (8) Å) instead of the 0.58-Å value found by Tilley. **18** can thus be considered as a sandwich compound, Ru(1) accommodating a Cp* group on one side and a ruthenacyclopentadiene ligand on the other.

The most anomalous aspect of complex **18** is its paramagnetism, especially since the yield of this product is quite good. It is formally a diruthenium 2.5 complex. We have been unable to isolate other derivatives out of the reaction mixture. The reaction is totally reproducible and the presence of adventitious oxygen very unlikely since for example [Cp*Ru(OMe)]$_2$, a quite air-sensitive product, is stable under our reaction conditions.

Conclusion

We have shown in this study that the Cp*Ru$^+$ fragment can coordinate selectively to an aromatic ring of functional arenes whatever function is present (carboxylic acid, phenol, olefin, carboxylate, phenate, ether, ester, disubstituted acetylene, etc.), except nitrile and terminal acetylene. The reaction with nitrile leads to mixtures of π- and σ-derivatives and even to loss of Cp*, a behavior that we have already observed upon reacting the Cp*Ru$^+$ fragment with pyridine. However, in the case of benzonitrile, it has not been possible to prepare selectively the π-adduct as in the case of pyridine. The Cp*Ru$^+$ fragment can stabilize anionic organic groups and thus lead to a zwitterionic benzoato derivative. In the case of phenol, the reactivity of the phenate complex (transfer of protons, alkylation) is also in favor of a substantial zwitterionic character. The reaction with phenylacetylene is the most complicated. As for benzonitrile, the reaction of Cp*Ru$^+$ with phenylacetylene leads to complicated mixtures, whereas that of [Cp*Ru(CH_3CN)$_3$](CF_3SO_3) leads to a paramagnetic dinuclear species following an unknown mechanism.

It is interesting to note that, in the conjugated systems containing two phenyl rings we have studied, the formation of the bis-ruthenium adduct is favored. This is apparently not the case for the polyaromatics studied by Koelle et al.[20] in which electrochemical studies show the two Cp*Ru(η^6-arene) units to be electronically well isolated (anthracene and pyrene). It is thus possible that ruthenium coordination to one ring electronically activates the other one in the case of conjugated systems. This would mean an electron-releasing effect of the ruthenium substituents, quite surprising when considering their cationic structure.

Finally, the preceding observations coupled to our recent demonstrations that Cp*Ru$^+$ can dehydrogenate C_5 or C_6 cyclic olefins without hydrogen acceptor[28] and also modify the electronic structure of quinones to obtain coordinated hydroquinone or TCNQ radicals[29] will make the use of this metal fragment attractive in different areas such as organic chemistry or material science.

Experimental Section

General Considerations. All manipulations were carried out under an argon atmosphere by using standard Schlenk tube techniques. Solvents were degassed before use; toluene, hexane, dichloromethane, and diethyl ether were freshly distilled before use. Arenes, NH_4PF_6, and CF_3SO_3H were obtained from commercial sources and were used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker WM 250, AC 200, or WH 90 spectrometer. Integration ratios were measured on one scan to avoid relaxation problems. IR spectra were recorded on a Perkin-Elmer 983 spectrometer. Elemental analyses were performed in the "Laboratoire de Chimie de Coordination du CNRS de Toulouse". Some of the ionic or zwitterionic complexes described were shown to cocrystallize with molecules of solvent. Phenol was unambiguously characterized in the case of **12** by ^1H and ^{13}C NMR, dichloromethane was also detected in NMR (δ 5.74 ppm in ^1H NMR in d^6-acetone) with a correct integration ratio in the case of **9**, and acetone was observed in NMR (δ 2.20 ppm in ^1H NMR in d^6-acetone) for **14**. **15** is shown to be associated with water in the disordered structure referred to as **15**; the presence of water in the microcrystals is thus reasonable. The presence of water, proposed in **11**, was not demonstrated by any other technique, but reproducible microanalytical data were observed and thus proposed.

[Cp*Ru(OMe)]$_2$ was prepared according to a published method.[22] It was extracted with dichloromethane, and this solution was used directly for the preparation of all other compounds without further purification. In the procedures described below, the stoichiometry was calculated assuming a 100% yield of this reaction.

[Cp*Ru(η^6-PhC≡CPh)](CF_3SO_3) (5). To a stirred dichloromethane solution (10 mL) of [Cp*RuOMe]$_2$ (0.32 mmol, 200 mg of [Cp*RuCl_2]$_n$) was added CF_3SO_3H (58 μL, 0.65 mmol). The color changed immediately from red to brown. The resulting mixture was added dropwise to a stirred solution of diphenylacetylene (174 mg, 0.98 mmol (excess)) in CH_2Cl_2(10 mL). The resulting mixture was stirred for another hour, and the color of the solution turned light brown. After the solvent was removed under reduced pressure, the brown residue was washed with diethyl ether (3 × 5 mL). The crude product was dissolved in dichloromethane and treated with diethyl ether to precipitate 292 mg (yield 81%) of white microcrystals of **5**. Anal. Calcd for $C_{25}H_{25}F_3O_3SRu$: C, 53.28; H, 4.47. Found: C, 53.12; H, 4.50.

[(Cp*Ru)$_2$(η^6,η^6-PhC≡CPh)](CF_3SO_3)$_2$ (6). Diphenylacetylene (58 mg, 0.32 mmol) in CH_2Cl_2 (5 mL) was added to a solution of CF_3SO_3H (58 μL, 0.65 mmol) and [Cp*Ru(OMe)]$_2$ (0.32 mmol, 200 mg of [Cp*RuCl_2]$_n$) in CH_2Cl_2, and the resulting solution was stirred for 1 h. **6** was obtained as white microcrystals upon recrystallization from CH_2Cl_2·Et_2O as before (263 mg, 85% yield). Anal. Calcd for $C_{36}H_{40}F_6O_6S_2Ru_2$: C, 45.57; H, 4.25. Found: C, 45.73; H, 4.31. Crystals suitable for X-ray analysis were obtained in this way.

[(Cp*Ru)$_2$(η^6,η^6-PhCH=CHPh)](PF_6)$_2$ (7). A methanol solution (15 mL) containing excess NH_4PF_6 (500 mg, 3 mmol) was added to a stirred homogeneous solution of *trans*-stilbene (117 mg, 0.65 mmol) and [Cp*Ru(OMe)]$_2$ (0.32 mmol, 200 mg of [Cp*RuCl_2]$_n$) in dichloromethane. The color changed immediately from red to light yellow, and a white powder precipitated. After stirring for an hour, the solvents were removed in vacuo, and the resulting solid was washed with dichloromethane (3 × 10 mL). A small amount of **8** was found in the dichloromethane solution (^1H NMR evidence). The residues obtained were washed with

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(29) Huang, Y. S.; He, X. D.; Chaudret, B.; Boubekeur, K.; Batail, P. Manuscript in preparation.

methanol (4 × 5 mL) and gave **7** as white microcrystals (285 mg, yield 83%). Anal. Calcd for $C_{34}H_{43}P_2F_{12}Ru_2$: C, 43.32; H, 4.49. Found: C, 42.66; H, 4.53.

Attempt To Prepare [Cp*Ru(η^6-PhCH=CHPh)](CF_3SO_3) (8). The procedures was as for **5**. A mixture of CF_3SO_3H (58 μL, 0.65 mmol) and $[Cp^*RuOMe]_2$ (0.32 mmol, 200 mg of $[Cp^*RuCl_2]_n$) in dichloromethane was added dropwise to a *trans*-stilbene solution (117 mg, 0.65 mmol) in the same solvent with stirring. The resulting solution turned light brown upon stirring for another hour. After removing the solvent under reduced pressure, the resulting brown residue was washed with diethyl ether (3 × 5 mL). The crude product was then dissolved in dichloromethane and treated with diethyl ether to precipitate white microcrystals. However, NMR and microanalytical data show that we obtain roughly a 0.7:0.3 mixture of **8** and **7**.

[(Cp*Ru)$_2$(η^6,η^6-PhCOPh)](CF_3SO_3)$_2$ (9). One equivalent of benzophenone (85 mg, 0.47 mmol) was added to a mixture of CF_3SO_3H (86 μL, 0.97 mmol) and $[Cp^*RuOMe]_2$ (0.48 mmol, 300 mg of $[Cp^*RuCl_2]_n$) in dichloromethane (10 mL), and the resulting solution was stirred for 2 h. **9**·$0.25CH_2Cl_2$ was obtained as pale yellow microcrystals upon recrystallization from CH_2Cl_2/Et_2O as before (405 mg, 88% yield). Anal. Calcd for $C_{35.25}H_{40.5}F_6O_7Cl_{0.5}Ru_2$: C, 43.46; H, 4.16. Found: C, 43.42; H, 3.81.

When the reaction was performed with 2 equiv of benzophenone to prepare **10, [Cp*Ru(η^6-PhCOPh)](CF_3SO_3)**, we have obtained **9** as major product and **10** was formed in less than 10% (spectroscopic) yield and not isolated.

[Cp*Ru(η^6-PhOH)](CF_3SO_3) (11). Phenol (92 mg, 0.98 mmol excess) in CH_2Cl_2 (10 mL) was added to a mixture of CF_3SO_3H (58 μL, 0.65 mmol) and $[Cp^*RuOMe]_2$ (0.32 mmol, 200 mg of $[Cp^*RuCl_2]_n$). **11**·$0.5H_2O$ was obtained as before as white microcrystals (276 mg, 87% yield). Anal. Calcd for $C_{17}H_{22}F_3O_{4.5}SRu$: C, 41.80; H, 4.54. Found: C, 41.77; H, 4.38.

[Cp*Ru(η^6-PhOCH$_3$)](CF_3SO_3) (13). The procedure was as before. Anisole (0.106 mL, 0.98 mmol) was added to a mixture of CF_3SO_3H (58 μL, 0.65 mmol) and $[Cp^*RuOMe]_2$ (0.32 mmol, 200 mg of $[Cp^*RuCl_2]_n$). **13** was obtained as white microcrystals (160 mg, 71% yield). Anal. Calcd for $C_{18}H_{23}F_3O_4SRu$: C, 43.81; H, 4.70. Found: C, 43.54; H, 4.57.

[Cp*Ru(η^6-PhCOOH)](CF_3SO_3) (14). Benzoic acid (120 mg, 0.98 mmol) in CH_2Cl_2 (10 mL) was added to a mixture of CF_3SO_3H (58 μL, 0.65 mmol) and $[Cp^*RuOMe]_2$ (0.32 mmol, 200 mg of $[Cp^*RuCl_2]_n$). The crude product was dissolved in acetone and treated with diethyl ether to precipitate white microcrystals of **14**·$0.5(CH_3)_2CO$ in 73% yield (250 mg). Anal. Calcd for $C_{19.5}H_{24}F_3O_{5.5}SRu$: C, 43.65; H, 4.51. Found: C, 43.59; H, 4.23.

[Cp*Ru(η^6-PhCOOCH$_3$)](CF_3SO_3) (16). The procedure was as for **5**. Methyl benzoate (0.122 mL, 0.98 mmol) was added to a mixture of CF_3SO_3H (58 μL, 0.65 mmol) and $[Cp^*Ru(OMe)]_2$ (0.32 mmol, 200 mg of $[Cp^*RuCl_2]_n$). **16** was obtained as white microcrystals in 64% yield (222 mg). Anal. Calcd for $C_{19}H_{23}F_3O_5SRu$: C, 43.76; H, 4.45. Found: C, 43.23; H, 4.46.

[Cp*Ru(η^6-PhO)]·2PhOH (12·2PhOH). Excess phenol (250 mg, 2.5 mmol) in methylene chloride was added to a pentane solution of $[Cp^*RuOMe]_2$ (0.32 mmol, 200 mg of $[Cp^*RuCl_2]_n$) with stirring. The color turned immediately from red to light brown, and a white product precipitated. After 1 h, the precipitate was filtered and washed with diethyl ether (3 × 5 mL), leaving **12**·2PhOH as white microcrystals (275 mg; yield 82%). Anal. Calcd for $C_{28}H_{32}O_3Ru$: C, 64.97; H, 6.23. Found: C, 64.56; H, 6.57.

Reactions of 12 with CH$_3$I and *i*-PrNH$_2$. Excess CH_3I was added to a dichloromethane solution of **12**·2PhOH, and the resulting solution was stirred at room temperature for 2 h. The solvent was then evaporated under reduced pressure. The crude product was washed with diethyl ether (2 × 5 mL) and identified as **13** by ^1H NMR. The reaction of **15** with CH_3I was carried out similarly.

The reaction of **12** with *i*-$PrNH_2$ was also carried out similarly. However, no reaction was observed for a period of a week, even when warming the solution.

[Cp*Ru(η^6-PhCOO)] (15). Benzoic acid (79 mg, 0.65 mmol) in CH_2Cl_2 (10 mL) was added to a stirred pentane solution of $[Cp^*RuOMe]_2$ (0.32 mmol, 200 mg of $[Cp^*RuCl_2]_n$). The color turned immediately from red to light brown, and a white product precipitated. After 1 h, the precipitate was filtered and washed with diethyl ether (3 × 5 mL), leaving **15** as white microcrystals (146 mg; yield 61%). Anal. Calcd for $C_{17}H_{22}O_3Ru$: C, 54.34; H, 5.86. Found: C, 54.25; H, 6.10. Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of **15** in methanol (15 mL) at room temperature for a week. This explains the presence of some π-methylbenzoato derivative in the disordered structure (**15′**).

Table VII. Summary of Crystal Data and Intensity Collection Parameters for [(Cp*Ru)$_2$(η^6,η^6-PhC≡CPh)](CF_3SO_3)$_2$ (6), 0.7{[Cp*Ru(PhCOO)]•2H$_2$O}•0.3{[Cp*Ru(PhCOOCH$_3$)]OH} (15′), and [Ru$_2$Cp*$_2$(PhC$_2$H$_2$)(MeCN)]CF$_3$SO$_3$ (18)

	6	15′	18
formula	$C_{36}H_{40}F_6O_6$-Ru_2S_2	$C_{17.3}H_{24}O_{3.7}Ru$	$C_{39}H_{45}F_3NO_3R_2S$
fw	949.0	392.2	867.0
cryst color, form	white translucent plate	light brown parallelepiped	deep brown plate
cryst syst	orthorhombic	monoclinic	orthorhombic
space group	*Pbca* (No. 61)	$P2_1/n$ (No. 14)	$Pca2_1$ (No. 29)
a, Å	11.363 (2)	7.4115 (9)	17.560 (3)
b, Å	14.262 (3)	14.233 (1)	12.521 (2)
c, Å	23.859 (3)	15.680 (2)	19.097 (3)
β, deg		93.29 (1)	
V, Å^3	3867 (2)	1651.3 (5)	4199 (2)
d_{calcd}, g/cm^3	1.63	1.58	1.37
Z	4	4	4
cryst dimens, mm	0.40 × 0.25 × 0.10	0.45 × 0.35 × 0.15	0.30 × 0.20 × 0.05
abs coeff (μ), cm^{-1}	9.4	9.4	8.0
radiation (λ, Å)	Mo Kα	(λ = 0.71073 Å)	
scan mode	ω–2θ	ω–2θ	ω–2θ
scan range, deg	0.70 + 0.35 tan θ	0.90 + 0.35 tan θ	1.00 + 0.35 tan θ
scan speed, deg/min	1.1–5.5	1.1–8.2	1.1–5.5
no. of data collcd	5012	3130	3808
transmiss coeff	0.70–1.00	0.81–1.00	0.92–1.00
no. of unique data	2610	2576 ($0kl$ and $0k\bar{l}$-merged, R_{av} = 0.009)	2869
obs criterion	$F_o^2 \geq 3\sigma(F_o^2)$	$F_o^2 \geq 3\sigma(F_o^2)$	$F_o^2 \geq 2\sigma(F_o^2)$

[Cp*Ru(CH$_3$CN)$_3$](CF_3SO_3) (17) was prepared by the protonation of $[Cp^*Ru(OMe)]_2$ in THF by HSO_3CF_3 in presence of CH_3CN and was used without purification.

[Cp*(CH$_3$CN)Ru(μ_2-η^2,η^4-C$_4$H$_2$Ph$_2$)RuCp*](CF_3SO_3) (18). To a THF solution (20 mL) of **17** (0.65 mmol, 200 mg of $[Cp^*RuCl_2]_n$) was added excess phenylacetylene (215 μL, 3 equiv) at −78 °C. The solution was allowed to warm to ambient temperature with stirring. At ca. 0 °C, a green precipitate began to form. After 2 h, the mixture was filtered and the resulting green precipitate was washed with diethyl ether (3 × 5 mL). The crude product was dissolved in methylene chloride and treated with diethyl ether to precipitate 292 mg (yield 81%) of green microcrystals of **18**. g = 2.1034. Anal. Calcd for $C_{39}H_{45}F_3O_3SNRu_2$: C, 54.03; H, 5.23; N, 1.62. Found: C, 53.95; H, 5.17; N, 1.43. The monocrystals for X-ray crystal structure determination were obtained by addition of THF over a CH_2Cl_2 solution of **18**.

X-ray Data Collection and Reduction. Crystal data and intensity collection parameters for **6**, **15**, and **18** are summarized in Table VII. Diffraction experiments were performed at 20 °C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo Kα radiation. A least-squares fit of 25 reflections ($18 < 2\theta < 26°$) was used to obtain the final lattice parameters and the orientation matrices for **6**, **15′**, and **18**, respectively. The observed extinctions were consistent with the space group *Pbca* for **6**, $P2_1/n$ for **15′**, and $Pca2_1$ for **18**. During data collection, of which the process is described elsewhere[30] ($3 < 2\theta < 60°$ for **6**, $+h,+k,+l$ data; $3 < 2\theta < 50°$ for **15′**, $+h,+k,+l$ data; $3 < 2\theta < 50°$ for **18**, $+h,+k,+l$ data), intensity data of three reflections were

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[30] Mosset, A.; Bonnet, J.-J.; Galy, J. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2639.

Table VIII. Fractional Atomic Coordinates and Equivalent Temperature Factors (Å² × 100) with Esd's in Parentheses for 6

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}[a]
Ru	0.22819 (2)	0.42373 (2	0.60446 (1)	3.53 (4)
C(1)	0.3388 (3)	0.3001 (2)	0.5972 (2)	4.0 (6)
C(2)	0.2996 (4)	0.3086 (3)	0.6529 (2)	4.6 (6)
C(3)	0.1748 (4)	0.3024 (3)	0.6537 (2)	4.6 (6)
C(4)	0.1350 (3)	0.2911 (2)	0.5973 (2)	4.1 (6)
C(5)	0.2370 (3)	0.2896 (2)	0.5619 (2)	4.0 (5)
C(6)	0.4646 (4)	0.2992 (3)	0.5789 (2)	6.3 (8)
C(7)	0.3774 (4)	0.3162 (3)	0.7041 (2)	6.1 (8)
C(8)	0.0942 (4)	0.3034 (3)	0.7034 (2)	6.3 (8)
C(9)	0.0108 (3)	0.2805 (3)	0.5776 (2)	5.5 (7)
C(10)	0.2375 (4)	0.2780 (3)	0.4993 (2)	6.2 (8)
C(11)	0.0369 (4)	0.5086 (3)	0.5156 (2)	5.9 (8)
C(12)	0.1276 (4)	0.5281 (2)	0.5568 (2)	5.0 (7)
C(13)	0.2470 (4)	0.5314 (2)	0.5402 (2)	5.4 (7)
C(14)	0.3389 (4)	0.5434 (3)	0.5796 (3)	6.0 (8)
C(15)	0.3080 (5)	0.5538 (2)	0.6355 (3)	7 (1)
C(16)	0.1885 (5)	0.5528 (2)	0.6523 (2)	6.6 (9)
C(17)	0.1012 (4)	0.5387 (3)	0.6124 (2)	5.9 (8)
S	0.3007 (2)	0.4994 (1)	0.36076 (8)	8.6 (3)
O(1)	0.3726 (4)	0.4661 (3)	0.4071 (2)	10 (1)
O(2)	0.3726 (4)	0.5367 (3)	0.3197 (2)	11 (1)
O(3)	0.1913 (4)	0.5433 (3)	0.3732 (2)	12 (1)
C(18)	0.2515 (6)	0.3955 (5)	0.3317 (2)	8 (1)
F(1)	0.1858 (4)	0.4093 (3)	0.2876 (1)	13.0 (9)
F(2)	0.3361 (4)	0.3461 (3)	0.3171 (2)	16 (1)
F(3)	0.1839 (4)	0.3497 (3)	0.3646 (2)	11.5 (8)

[a] Equivalent isotropic U_{eq} values are defined as one-third of the trace of the U_{ij} tensor.

Table IX. Fractional Atomic Coordinates and Isotropic or Equivalent Temperature Factors (Å² × 100) with Esd's in Parentheses for 15′

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}/U_{iso}[a]
Ru	0.55696 (4)	0.26003 (2)	0.41498 (2)	2.80 (5)
C(1)	0.7995 (5)	0.3417 (3)	0.3962 (2)	3.6 (6)
C(2)	0.8436 (5)	0.2621 (3)	0.4485 (3)	4.0 (6)
C(3)	0.8042 (5)	0.1792 (3)	0.3998 (3)	3.9 (6)
C(4)	0.7321 (5)	0.2076 (3)	0.3177 (2)	3.7 (6)
C(5)	0.7293 (5)	0.3078 (3)	0.3151 (2)	3.5 (6)
C(6)	0.8259 (7)	0.4433 (3)	0.4188 (3)	6.0 (9)
C(7)	0.9226 (6)	0.2662 (4)	0.5392 (3)	6.2 (9)
C(8)	0.8416 (7)	0.0795 (4)	0.4261 (4)	7 (1)
C(9)	0.6779 (8)	0.1436 (3)	0.2452 (3)	6.2 (9)
C(10)	0.6741 (7)	0.3670 (3)	0.2388 (3)	5.4 (8)
C(11)	0.2880 (5)	0.1929 (3)	0.3947 (3)	4.2 (7)
C(12)	0.3637 (6)	0.1672 (3)	0.4764 (3)	4.6 (7)
C(13)	0.4227 (6)	0.2365 (3)	0.5355 (3)	4.6 (7)
C(14)	0.4067 (5)	0.3320 (3)	0.5137 (3)	4.5 (7)
C(15)	0.3298 (5)	0.3579 (3)	0.4324 (3)	4.4 (7)
C(16)	0.2703 (5)	0.2893 (3)	0.3725 (3)	3.9 (6)
C(17)	0.1985 (6)	0.3187 (3)	0.2842 (3)	4.8 (7)
O(1)	0.1645 (6)	0.2563 (2)	0.2307 (2)	6.9 (7)
O(2)	0.1775 (6)	0.4055 (3)	0.2727 (2)	7.2 (7)
Ow(1)	0.3633 (9)	0.5710 (3)	0.3262 (3)	11 (1)
H1(w1)	0.343 (9)	0.627 (2)	0.292 (3)	11 0
*H2(w1)	0.297 (8)	0.519 (2)	0.299 (3)	11 0
*Ow(2)	0.160 (10)	0.4660 (4)	0.156 (3)	9 (1)
*C(18)	0.1621 (21)	0.4401 (10)	0.1795 (4)	5.1 (4)

[a] Equivalent isotropic U_{eq} values are defined as one-third of the trace of the U_{i4}j tensor. * denotes occupancy factors of 0.7 for Hw(w1) and Ow(2) atoms and of 0.3 for C(18) atom.

Table X. Fractional Atomic Coordinates and Isotropic or Equivalent Temperature Factors (Å² × 100) with Esd's in Parentheses for 18[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}/U_{iso}
Ru(1)	0.45241 (3)	0.21767 (5)	3/4	3.01 (9)
Ru(2)	0.52265 (3)	0.27974 (5)	0.86656 (4)	2.80 (8)
C(1)	0.3384 (3)	0.1364 (4)	0.7548 (3)	3.2 (2)
C(2)	0.3310 (3)	0.2448 (4)	0.7341 (3)	2.7 (2)
C(3)	0.3662 (3)	0.2568 (4)	0.6676 (3)	4.9 (3)
C(4)	0.3954 (3)	0.1558 (4)	0.6472 (3)	4.6 (3)
C(5)	0.3782 (3)	0.0813 (4)	0.7010 (3)	5.0 (3)
C(6)	0.3074 (6)	0.0869 (9)	0.8201 (6)	7 (2)
C(7)	0.2890 (5)	0.3324 (7)	0.7735 (5)	6 (2)
C(8)	0.3709 (5)	0.3593 (7)	0.6261 (5)	6 (2)
C(9)	0.4386 (5)	0.1303 (7)	0.5819 (5)	4 (2)
C(10)	0.3968 (6)	−0.0353 (7)	0.7012 (6)	6 (2)
C(11)	0.6420 (3)	0.3467 (4)	0.8753 (2)	3.0 (2)
C(12)	0.6514 (3)	0.2424 (4)	0.9032 (2)	2.9 (2)
C(13)	0.6040 (3)	0.2332 (4)	0.9631 (2)	4.5 (3)
C(14)	0.5652 (3)	0.3317 (4)	0.9722 (2)	4.0 (3)
C(15)	0.5887 (3)	0.4019 (4)	0.9179 (2)	2.9 (2)
C(16)	0.6822 (5)	0.3891 (8)	0.8129 (5)	6 (2)
C(17)	0.7031 (5)	0.1543 (8)	0.8758 (6)	6 (2)
C(18)	0.5992 (6)	0.1377 (9)	0.0112 (5)	7 (2)
C(19)	0.5106 (5)	0.3575 (7)	1.0303 (5)	5 (2)
C(20)	0.5621 (6)	0.5154 (8)	0.9094 (6)	7 (2)
C(21)	0.5472 (5)	0.1395 (6)	0.8047 (4)	4 (1)
C(22)	0.5648 (4)	0.1648 (6)	0.7391 (4)	3 (1)
C(23)	0.5619 (4)	0.2697 (6)	0.7184 (4)	4 (1)
C(24)	0.5299 (4)	0.3332 (5)	0.7635 (4)	3 (1)
C(25)	0.5299 (2)	0.0356 (4)	0.8227 (2)	3.2 (2)
C(26)	0.5812 (2)	−0.0450 (4)	0.8161 (2)	3.8 (2)
C(27)	0.5725 (2)	−0.1472 (4)	0.8441 (2)	3.5 (2)
C(28)	0.5123 (2)	−0.1687 (4)	0.8897 (2)	5.2 (3)
C(29)	0.4610 (2)	−0.0880 (4)	0.9073 (2)	5.8 (3)
C(30)	0.4697 (2)	0.0141 (4)	0.8793 (2)	4.7 (3)
C(31)	0.5288 (3)	0.4494 (4)	0.7521 (3)	4.4 (2)
C(32)	0.5770 (3)	0.5061 (4)	0.7075 (3)	3.6 (2)
C(33)	0.5637 (3)	0.6141 (4)	0.6946 (3)	4.8 (3)
C(34)	0.5022 (3)	0.6655 (4)	0.7263 (3)	6.0 (3)
C(35)	0.4540 (3)	0.6088 (4)	0.7709 (3)	7.2 (4)
C(36)	0.4673 (3)	0.5007 (4)	0.7838 (3)	6.2 (3)
N	0.4098 (4)	0.2891 (6)	0.9005 (3)	4 (1)
C(37)	0.3550 (5)	0.2959 (7)	0.9374 (5)	5 (2)
C(38)	0.2939 (6)	0.3052 (8)	0.9900 (6)	7 (2)
*S(1)	0.6437 (2)	0.3752 (3)	0.4943 (2)	2.3 (6)
*O(1)	0.5766 (8)	0.3529 (12)	0.5288 (8)	5 (3)
*O(2)	0.6375 (10)	0.4647 (15)	0.4536 (10)	7 (4)
*O(3)	0.6655 (8)	0.2901 (14)	0.4503 (9)	6 (3)
*C(39)	0.7223 (12)	0.3942 (18)	0.5589 (11)	4 (4)
*F(1)	0.7270 (9)	0.3118 (11)	0.5952 (9)	8 (3)
*F(2)	0.7053 (9)	0.4773 (12)	0.5968 (8)	7 (3)
*F(3)	0.7849 (7)	0.4122 (10)	0.5282 (6)	5 (2)
*S(2)	0.1462 (2)	0.1108 (3)	0.6015 (2)	3.1 (7)
*O(4)	0.1165 (8)	0.1452 (11)	0.5374 (9)	5 (3)
*O(5)	0.1869 (8)	0.1930 (13)	0.6303 (9)	5 (3)
*O(6)	0.0880 (9)	0.0777 (12)	0.6441 (8)	5 (3)
*V(40)	0.2091 (14)	−0.0018 (20)	0.5798 (15)	6 (5)
*F(4)	0.2709 (7)	0.0309 (10)	0.5520 (7)	5 (2)
*F(5)	0.1753 (9)	−0.0726 (12)	0.5493 (10)	8 (3)
*F(6)	0.2303 (10)	−0.0404 (13)	0.6440 (10)	9 (4)

[a] Equivalent isotropic U_{eq} values are defined as one-third of the trace of the $U_{i,j}$ tensor. * denotes occupancy factors of 0.5.

monitored every 2 h. Their intensities showed only random, statistical fluctuations. The data were reduced in the usual day with the SDP[31] package. An empirical absorption correction was applied to each data set on the basis of four ψ scans.

Structure Solution and Refinement. Non-hydrogen atomic scattering factors (f', f'') were taken from ref 33, hydrogen ones from ref 34. In all cases, heavier atom positions were determined by direct methods, using the SHELXS-86 program.[35] The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. Refinements were carried out with the

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(35) Sheldrick, G. M. SHELXS 86, Program for Crystal Structure Solution; University of Göttingen: Göttingen, Federal Republic of Germany, 1986.

SHELX-76 program[36] by using full-matrix least-squares techniques of F_o, minimizing the function $\sum w(|F_o| - |F_c|)^2$.

$[(Cp^*Ru)_2(\eta^6,\eta^6\text{-PhC}{\equiv}\text{CPh})](CF_3SO_3)_2$ (6). All non-hydrogen atoms were refined anisotropically. All H atoms were observed but introduced in calculations in constrained geometry (C–H = 0.97 Å) with a general isotropic temperature factor, first refined, and then kept fixd to 0.06 Å. The refinement converged to R = 0.030 and R_w = 0.037 with a maximum shift/esd of 0.010 on the final cycle (mean value: 0.003) with 235 variable parameters. A fit of S = 1.19 for the data using the weighting scheme $w = [\sigma^2(F_o) + 0.0004F_o^2]^{-1}$ was obtained. The maximum residual peak was near the Ru atom at 0.7 e/Å^3. Fractional atomic coordinates are given in Table VIII.

$0.7\{[Cp^*Ru(PhCOO)]\cdot 2H_2O\}0.3\{[Cp^*Ru(PhCOOCH_3)]OH\}$ (15′). All non-hydrogen atoms of the [Cp*Ru(PhCOO)] entity were refined anisotropically. The two important residuals were first considered as water molecules and refined so. The subsequent difference-Fourier showed unambiguously H atoms of the Cp* and Ph groups, which were introduced in calculations with constrained geometry (C–H = 0.97 Å) with general isotropic temperature factors, first refined, and then kept fixed to 0.11 and 0.042 Å^2, respectively. Near the Ow(1) atom, two H atoms could be located, one of them being clearly at a lower height than the other one. Near the Ow(2) atom, there was a residual of about 1.8 e/Å^3 that could not be attributed to one H atom only. After distance calculations and chemical experiments, it appeared that the most suitable explanation was a disorder between a methyl and a water molecule. Occupancy factors of Ow(2) and C(18) methyl carbon were refined and then kept fixed to 0.70 and 0.30, respectively. Ow(2) was refined anisotropically, C(18) isotropically. No H atom was introduced on these two atoms. The H atoms near Ow(1) were refined, first with occupancy factors 1.0 and free isotropic thermal parameters. To obtain the same U value of 0.11 Å^2, occupancy factors were 1.0 for H1(w1) and 0.7 for H2(w1). It may be assumed that the 70% Ow(1) water molecule and the 30% OH$^-$ anion are not discernible. Ow(1) was refined anisotropically. It is noteworthy that the U_{11} component of Ow(1) and Ow(2) atoms is higher than the other two. The refinement converged to R = 0.032 and R_w = 0.042 with a maximum shift/esd of 0.113 (a H parameter) on the final cycle (mean value 0.007) with 209 variable parameters. A fit of S = 1.15 for the data using the weighting scheme $w = [\sigma^2(F_o) + 0.00035F_o^2]^{-1}$ was obtained. The maximum residual peak was between the Ow(2) and C(18) atoms at 0.8 e/Å^3. Fractional atomic coordinates are given in Table IX.

$[Ru_2(Cp^*)_2(PhC_2H)_2(MeCN)](CF_3SO_3)$ (18). Cp* and Ph rings were refined as isotropic rigid groups (C–C = 1.420 and 1.395 Å, respectively). All other non-hydrogen atoms were refined anisotropically, the occupancy factors of the two CF_3SO_3 entities having been first refined and then kept fixed to 0.5. All H atoms were introduced in calculated positions (C–H = 0.97 Å) with isotropic thermal parameters kept fixed to 0.07 Å^2 for methyl groups, 0.065 Å^2 for phenyl groups, and 0.05 Å^2 for C_2H_2 groups. Both enantiomers were tested and the best one kept (Hamilton test,[37] R-factor ratio = 1.08, significance level α = 0.01). The refinement converged to R = 0.036 and R_w = 0.038 with a maximum shift/esd of 0.08 (a F thermal parameter) on the final cycle (mean value 0.009) with 361 variable parameters. A fit of S = 1.22 for the data using the weighting scheme $w = [\sigma^2(F_o) + 0.0018F_o^2]^{-1}$ was obtained. The maximum residual peak was near the C(20) atom at 0.4 e/Å^3. Fractional atomic coordinates are given in Table X.

Supplementary Material Available: Tables listing fractional and hydrogen atomic coordinates, equivalent temperature factors, thermal parameters, and bond lengths and angles for compounds listed in the text (20 pages); tables listing observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

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(36) Sheldrick, G. M. SHELX 76, Program for Crystal Structure Determination; University of Cambridge, England, 1976.

(37) In ref 33, p 288.

Cyclopentadienyl(allyl)(butadiene)hafnium Compounds. Synthesis, Crystal Structure, and Dynamics of Cyclopentadienyl(1,2,3-trimethylallyl)(1,2-dimethylbutadiene)hafnium and Cyclopentadienyl(1,1,2-trimethylallyl)(2,3-dimethylbutadiene)hafnium

Thomas J. Prins, Bryan E. Hauger, Peter J. Vance, Michael E. Wemple, David A. Kort,
Jonathan P. O'Brien, and Michael E. Silver*

Department of Chemistry, Hope College, Holland, Michigan 49423

John C. Huffman

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Received July 19, 1990

The reaction of $CpHfCl_3\cdot 2THF$ with 2 equiv of (1,2,3-Me_3allyl)MgBr or (1,1,2-Me_3allyl)MgBr yields Cp(1,2,3-Me_3allyl)(1,2-Me_2butadiene)Hf (**3**) or Cp(1,1,2-Me_3allyl)(2,3-Me_2butadiene)Hf (**4**). X-ray crystallography of **3** shows that both the allyl and butadiene ligands assume a prone orientation with respect to Cp. For **3**: cell constants a = 15.109 (5), b = 7.150 (2), c = 15.587 (6) Å, β = 115.41 (1)°; space group $P2_1/c$; R = 0.0305, R_w = 0.0347. Variable-temperature ^1H NMR studies indicate that compound **3** is static on the NMR time scale whereas **4** exists in two isomeric forms and undergoes three separate dynamic processes involving η^3–η^1 isomerization at the unsubstituted and substituted ends of the allyl ligand [ΔG^* = 39.4 ± 1.0 kJ/mol and 73.4 ± 1.0 kJ/mol, respectively] and butadiene flip [ΔG^*(avg) = 49.8 ± 1.0 kJ/mol].

Introduction

Early transition metal compounds possessing allyl and/or butadiene ligands differ substantially from those whose only π ligand is cyclopentadienide (Cp). Allyl and butadiene ligands provide low barriers for a number of dynamic processes[1-3] and decomposition routes[4,5] not

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