Carbon−Carbon Bond Formation Promoted by Organoruthenium Complexes. The First Unsubstituted π-Metallabenzene Complex, $Cp^*_2Ru_2(\eta^2{:}\eta^5\text{-}C_5H_5)(SiMe_3)$, and Synthesis of the Tetramethyleneethane Complex $Cp^*_2Ru_2(\eta^3{:}\eta^3\text{-}C_6H_8)Cl_4$

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Received September 9, 1996[⊗]

Treatment of the methylene/silyl complex $Cp^*_2Ru_2(\mu\text{-}CH_2)(SiMe_3)(\mu\text{-}Cl)$ with ethyne in toluene gives several products resulting from carbon−carbon bond coupling reactions; these include the first unsubstituted π-metallabenzene complex, $Cp^*_2Ru_2(\eta^2{:}\eta^5\text{-}C_5H_5)(SiMe_3)$, **1**, the arene complex $[Cp^*Ru(\eta^6\text{-}C_6H_6)]Cl$, **2**, and the bridging metallacyclopentadiene complex $Cp^*_2Ru_2(\eta^2{:}\eta^4\text{-}C_4H_4)Cl_2$, **3**. Treatment of $[Cp^*RuCl_2]_2$ with propadiene also leads to a carbon−carbon bond coupling reaction, and the product is the tetramethyleneethane (i.e., 2,2′-biallyl) complex $Cp^*_2Ru_2(\eta^3{:}\ \eta^3\text{-}C_6H_8)Cl_4$, **4**. A single-crystal X-ray diffraction study of **1** shows that the metallabenzene ring is π-bonded to a second metal center and that the trimethylsilyl group is a terminal ligand on the ruthenium center that lies in the metallabenzene ring plane. The aromaticity of the metallabenzene ring in **1** is also discussed.

Introduction

Metallabenzene (or metallacyclohexatriene) rings are some of the most interesting metallacycles of the transition elements: they have been implicated as intermediates en route to a variety of cyclopentadienyl complexes,[1−4] and similar structures have been implicated as intermediates in alkyne oligomerization processes.[5−7] Also of fundamental interest is whether such metallabenzenes exhibit aromatic properties.[8] To date, relatively few metallabenzene complexes have been described. Stable sulfide- or thiol-substituted osmabenzene complexes have been obtained via a cyclization reaction from two molecules of acetylene and an osmium-thiocarbonyl complex.[9,10] Several dimethyl-substituted metallabenzene complexes have been prepared by α-H abstraction from the two terminal carbon centers of 2,4-dimethylpentadienyl groups.[11−17] Intermediates thought to be oxido- and alkoxy-substituted metallabenzene complexes have also been generated by attack of a dienediyl group on a carbonyl ligand; the dienediyl group can be in the form of an external reagent, such as a dilithiobutadiene, or as an internal reagent generated by lithiation of a coordinated σ-dienyl group.[2,3,18,19] Some dimetallabenzene complexes have also been described.[20] In all of these molecules, at least one of the carbon atoms of the metallabenzene ring bears a non-hydrogen substituent.

We have investigated the reactions of $Cp^*_2Ru_2(\mu\text{-}CH_2)(SiMe_3)(\mu\text{-}Cl)$ with ethyne and have been able to isolate several products resulting from carbon−carbon coupling reactions. We now describe the isolation and X-ray crystal structure of the first unsubstituted π-metallabenzene complex $Cp^*_2Ru_2(\eta^2{:}\eta^5\text{-}C_5H_5)(SiMe_3)$, in which the metallabenzene ring is π-bound to the second ruthenium center. The synthesis of this complex from a metal alkylidene and two equiv of an alkyne represents a new synthetic route to metallabenzene complexes. The presence of an unsubstituted metallabenzene ring in this compound provides a unique opportunity for probing the aromaticity of the ring by NMR spectroscopic and X-ray crystallographic techniques. We have also investigated the reaction of $[Cp^*RuCl_2]_2$ with propadiene, which yields an unusual tetramethyleneethane diruthenium complex $Cp^*_2Ru_2(\eta^3{:}\ \eta^3\text{-}C_6H_8)Cl_4$ through the carbon-centered coupling of two propadiene

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[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1997.

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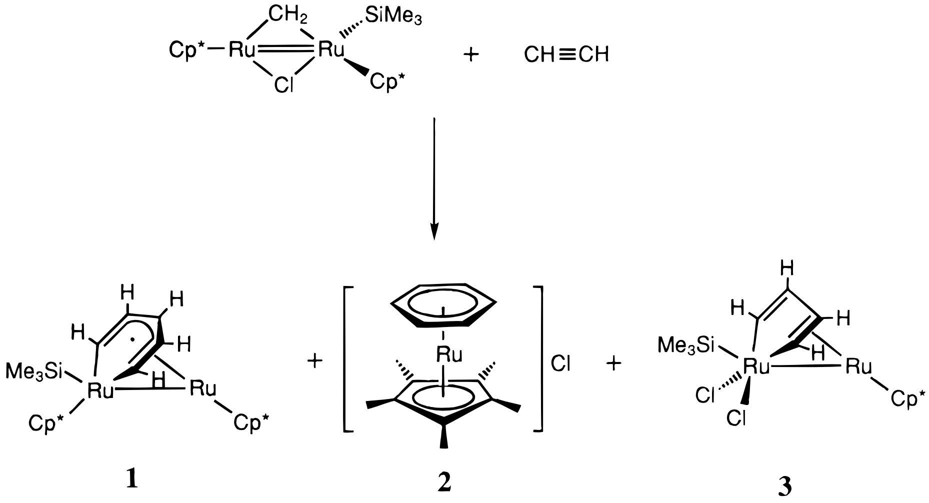
S0276-7333(96)00772-8 CCC: $14.00

Scheme 1. Reaction of $Cp^*{}_2Ru_2(\mu\text{-}CH_2)(SiMe_3)(\mu\text{-}Cl)$ with Ethyne



molecules. A preliminary account of some of these results has appeared.[21]

Results

Synthesis of the First Unsubstituted Metallabenzene Complex $Cp^*{}_2Ru_2(\eta^2{:}\eta^5\text{-}C_5H_5)(SiMe_3)$, 1. Treatment of the diruthenium methylene complex $Cp^*{}_2Ru_2(\mu\text{-}CH_2)(SiMe_3)(\mu\text{-}Cl)$[22] with HCCH in toluene at −78 °C followed by warming to room temperature gives three products which have been isolated in analytically pure form (Scheme 1). By cooling the saturated pentane extract of the reaction mixture to −20 °C, dark red crystals are obtained, which have been identified as the complex $Cp^*{}_2Ru_2(\eta^2{:}\eta^5\text{-}C_5H_5)(SiMe_3)$, **1**. As we will show, the C_5H_5 unit and one ruthenium center form a metallabenzene ring which is π-complexed to the second ruthenium center.

The ^1H NMR spectrum of **1** exhibits resonances at δ 9.75 (dd, $^3J_{HH} = 6.0$ Hz, $^4J_{HH} = 1.0$ Hz), 4.94 (dd, $^3J_{HH} = 7.0$ Hz, $^4J_{HH} = 6.0$ Hz), and 4.32 (tt, $^3J_{HH} = 7.0$ Hz, $^4J_{HH} = 1.0$ Hz) for the ortho, meta, and para protons of the ruthenabenzene ring, respectively (Figure 1a). The ^{13}C NMR spectrum of **1** shows resonances for the ruthenabenzene ortho, meta, and para carbons at δ 177.0, 86.8, and 83.4, respectively (Figure 2a). The two Cp* rings are inequivalent.

Although metallabenzenes are often reactive,[1−3,18,19,23] compound **1** is quite robust. It is air-stable and does not react with excess PMe_3 in refluxing benzene. Presumably, the stability of **1** in part reflects the fact that the RuC_5H_5 ring is bound to a second Ru center.

The metallabenzene ring arises from the coupling of the methylene ligand in $Cp^*{}_2Ru_2(\mu\text{-}CH_2)(SiMe_3)(\mu\text{-}Cl)$ to two molecules of ethyne; at some point, one of the two hydrogen atoms of the methylene ligand is lost, evidently as HCl. In order to gain insight into the mechanism by which the metallabenzene ring is formed, we treated $Cp^*{}_2Ru_2(\mu\text{-}CH_2)(SiMe_3)(\mu\text{-}Cl)$ with ethyne-d_2, DCCD, in toluene. Analysis shows that the d_4 isotopolog $Cp^*{}_2Ru_2(\eta^2{:}\eta^5\text{-}C_5HD_4)(SiMe_3)$ is obtained. ^1H and $^{13}C\{^1H\}$ NMR spectra show that one of the two hydrogen atoms of the bridging methylene group is retained in the product and that it appears in one of the two ortho positions of the ruthenabenzene ring (Figures 1b and 2b).

The labeling experiment gives information about the sequence of chemical events that leads to the formation of the metallabenzene ring. As stated above, one of the two hydrogen atoms on the methylene ligand is lost; this step could occur before reaction with the first equivalent of ethyne, after reaction with the first equivalent of ethyne, or after reaction with the second equivalent of ethyne. In the first two cases, a three-carbon chain having the labeling pattern Ru−CH−CD−CD−Ru will be formed. If this chain is symmetrically bound to the metal centers (possibly as a metallacyclobutadiene complex), then insertion of the second equivalent of ethyne could occur into either one of the Ru−C bonds; this would lead to a metallabenzene in which the hydrogen label would appear in *both* the ortho and para positions. The experimentally-observed *absence* of hydrogen in the para position of the ruthenabenzene ring suggests that elimination of HCl takes place *after* the insertion of two acetylene molecules into the $Ru−CH_2−Ru$ unit of the methylene/silyl complex.

The deuteration study also shows that there is a significant secondary isotope effect on the ^{13}C NMR chemical shifts of the ortho carbons: in Figure 2b, the peak for the *ortho*-CD group is shifted upfield from the peak for the *ortho*-CH group by 0.49 ppm. By comparing the ^{13}C NMR chemical shifts of the deuterated and undeuterated compounds, we find that deuteration of the meta and para carbons also shields these peaks by about 0.4 ppm. For comparison, the secondary isotope effect seen in the ^{13}C NMR spectrum upon complete deuteration of benzene is 0.55 ppm.[24] The similarity of this value to those we observe lends support to the idea that the metallabenzene ring in **1** is in fact aromatic.

Two other compounds have also been isolated from the reaction of $Cp^*{}_2Ru_2(\mu\text{-}CH_2)(SiMe_3)(\mu\text{-}Cl)$ and ethyne (Scheme 1). Addition of Et_2O to the CH_2Cl_2 extract of the reaction mixture induces the formation of an orange-red precipitate. Elemental analysis and ^1H and ^{13}C NMR spectra establish this product to be the known[25,26] arene complex $[Cp^*Ru(\eta^6\text{-}C_6H_6)]Cl$, **2**. Cooling the CH_2-

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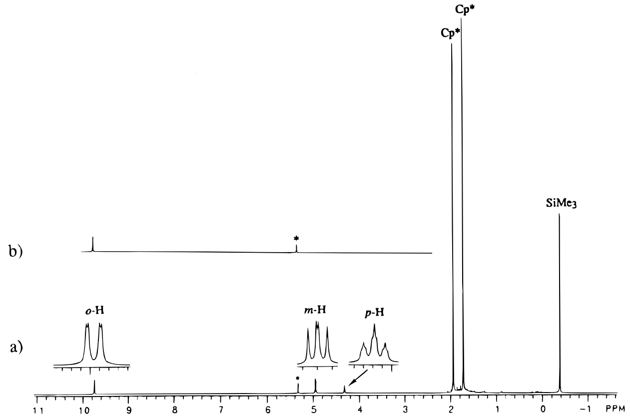

Figure 1. (a) 500 MHz ^1H NMR spectrum of $Cp^*{}_2Ru_2(\eta^2,\eta^5\text{-}C_5H_5)(SiMe_3)$ in CH_2Cl_2 at 25 °C. (b) 500 MHz ^1H NMR spectrum of $Cp^*{}_2Ru_2(\eta^2,\eta^5\text{-}C_5HD_4)(SiMe_3)$ in CH_2Cl_2 at 25 °C.

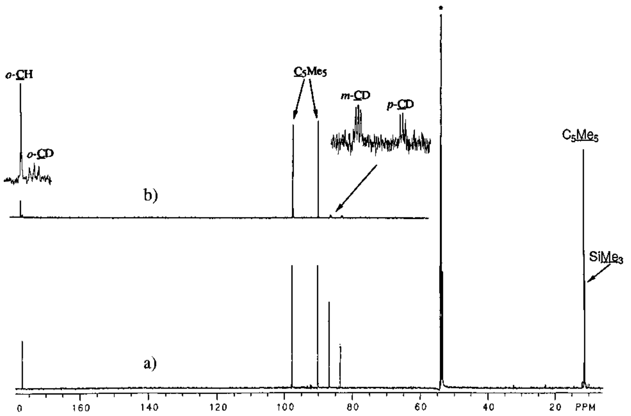

Figure 2. (a) 125 MHz $^{13}C\{^1H\}$ NMR spectrum of $Cp^*{}_2Ru_2(\eta^2{:}\eta^5\text{-}C_5H_5)(SiMe_3)$ in CH_2Cl_2 at 25 °C. (b) 125 MHz $^{13}C\{^1H\}$ NMR spectrum of $Cp^*{}_2Ru_2(\eta^2{:}\eta^5\text{-}C_5HD_4)(SiMe_3)$ in CH_2Cl_2 at 25 °C.

Cl_2/Et_2O filtrate to −20 °C yielded red crystals of a third compound, which has been shown by elemental analysis and ^1H and ^{13}C NMR spectroscopy to be the known[27] bridging metallacyclopentadiene complex $Cp^*{}_2Ru_2(\eta^2{:}\eta^4\text{-}C_4H_4)Cl_2$, **3**.

Although we do not have any information about the reaction mechanisms responsible for the formation of **2** and **3**, these results clearly show that the methylene/silyl complex $Cp^*{}_2Ru_2(\mu\text{-}CH_2)(SiMe_3)(\mu\text{-}Cl)$ readily engages in carbon−carbon bond forming reactions with alkynes. This is consistent with the reactions of alkynes with bridging alkylidene complexes of ruthenium studied by Knox and co-workers.[5−7]

X-ray Crystal Structure of 1. A single-crystal X-ray diffraction study has been performed in order to confirm the structure of **1**. Single crystals of **1**, grown from pentane at −20 °C, crystallize in the orthorhombic space group *Pnma* with four molecules in the unit cell. The molecule has a symmetry plane that passes through Ru(1), Ru(2), and the centers of all of the ligands. Figure 3 shows an ORTEP drawing of **1**. Crystal data are collected in Table 1, and selected bond distances and angles are listed in Table 2.

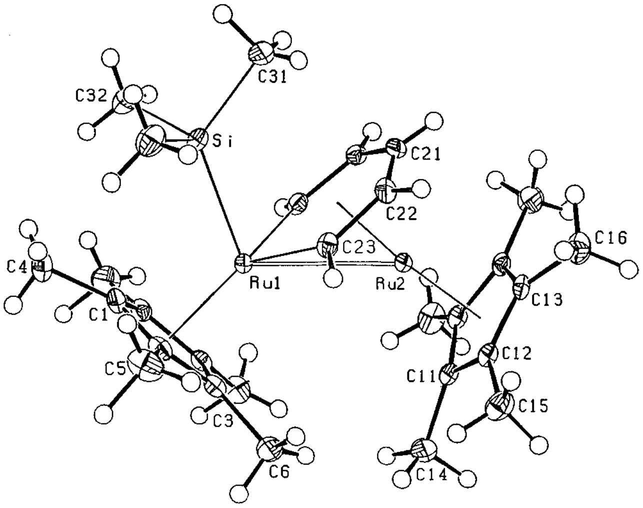

Figure 3. ORTEP diagram of $Cp^*{}_2Ru_2(\eta^2{:}\eta^5\text{-}C_5H_5)(SiMe_3)$. The ellipsoids represent the 35% probability density surfaces, except for hydrogen atoms which are represented by arbitrarily-sized spheres.

Table 1. Crystal Data for $Cp^*{}_2Ru_2(\eta^2{:}\eta^5\text{-}C_5H_5)(SiMe_3)$, 1, at −75 °C

space group: *Pnma*	$V = 2671(2)$ Å^3
$a = 21.973(7)$ Å	$Z = 4$
$b = 13.676(4)$ Å	$d_{calcd} = 1.519$ g cm^{-3}
$c = 8.888(4)$ Å	$\mu_{calcd} = 11.67$ cm^{-1}
$\beta = 90°$	size: 0.2 × 0.5 × 0.5 mm

diffractometer: Enraf-Nonius CAD4
radiation: Mo Kα, $\lambda = 0.710\,73$ Å
monochromator: graphite crystal, $2\theta = 12°$
scan range, type: $2.0° < 2\theta < 48.0°$, ω/θ
scan speed, width: 3−16° min^{-1}, $\Delta\omega = 1.50[1.10 + 0.35 \tan \theta]°$
no. of rflcns: 4210 total, 2723 unique, 2350 with $I > 2.58\sigma(I)$
internal consistency, $R_i = 0.015$

$R_F = 0.023$	no. of variables: 247
$R_{wF} = 0.027$	*p* factor: 0.010

Table 2. Bond Distances and Angles for $Cp^*{}_2Ru_2(\eta^2{:}\eta^5\text{-}C_5H_5)(SiMe_3)$, 1[a]

Bond Distances (Å)

Ru(1)−Ru(2)	2.8983(3)	C(21)−C(22)	2.417(3)
Ru(1)−Si	2.426(1)	C(22)−C(23)	1.406(4)
Ru(1)−C(23)	1.970(3)	C(1)−C(2)	1.418(3)
Ru(1)−C(1)	2.320(4)	C(2)−C(3)	1.413(4)
Ru(1)−C(2)	2.303(3)	C(3)−C(3)′	1.437(3)
Ru(1)−C(3)	2.218(2)	C(11)−C(12)	1.415(3)
Ru(2)−C(11)	2.275(4)	C(12)−C(13)	1.431(4)
Ru(2)−C(12)	2.218(3)	C(13)−C(13)′	1.422(3)
Ru(2)−C(13)	2.164(2)	C(21)−H(21)	0.82(5)
Ru(2)−C(21)	2.134(4)	C(22)−H(22)	0.93(3)
Ru(2)−C(22)	2.175(3)	C(23)−H(23)	0.99(3)
Ru(2)−C(23)	2.290(3)		

Bond Angles (deg)

Si−Ru(1)−Cn(1)	115.8(1)	C(23)−Ru(1)−C(23)′	89.0(1)
Si−Ru(1)−C(23)	83.90(8)	Ru(1)−C(23)−C(22)	129.0(2)
Cn(1)−Ru(1)−C(23)	132.91(8)	C(21)−C(22)−C(23)	123.2(3)
Cn(11)−Ru(2)−Cn(21)	159.3(2)	C(22)−C(21)−C(22)′	124.1(3)

[a] Cn represents the centroid of a ring, and the index is that of the lowest indexed carbon atom in the ring.

Molecules of **1** consist of two ruthenium centers connected by a single dative Ru−Ru bond with a Ru(1)−Ru(2) distance of 2.898(1) Å (Figure 3); alternatively, **1** can be formulated as a zwitterionic species with a single Ru−Ru bond to achieve 18-electron counts on both ruthenium centers. One of the ruthenium atoms, Ru(1), is η^5-bonded to a Cp* group, σ-bonded to the $SiMe_3$ group (Ru(1)−Si = 2.426(1) Å), and forms the sixth vertex of the metallabenzene ring; the two Ru(1)−C distances of 1.970(3) Å to the metallabenzene ring are shorter than expected for a single bond (2.05−2.19 Å) and suggest that there is partial metal−carbon π-bonding.[28] The C_{ortho}−Ru(1)−C_{ortho} angle of 89.0(1)°

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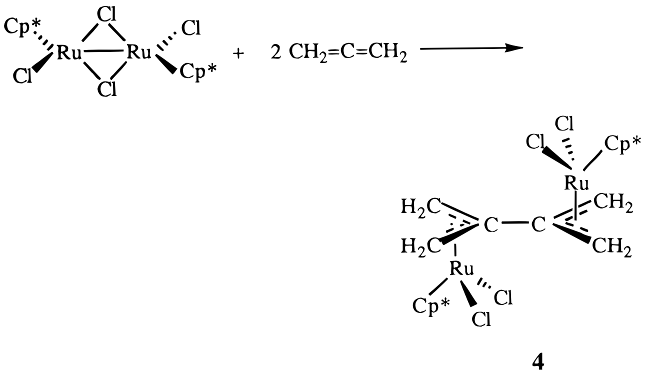
is similar to that found in other heterobenzenes; for example, the C−Sb−C bond angle in stibabenzene is 93°.[29] In fact, this C_{ortho}−Ru(1)−C_{ortho} angle is well within the observed range of 84.7−92.4° for other known metallabenzene rings.[9,11,14−17] The second ruthenium atom in the compound, Ru(2), is η^5-bound to the other Cp* group and is π-bonded to the RuC_5H_5 ruthenabenzene ring: the Ru(2)−C distances to the metallabenzene ring are 2.290(3), 2.175(3), and 2.134(4) Å for the ortho, meta, and para carbon atoms, respectively.

The C_{ortho}−C_{meta} and C_{meta}−C_{para} bond distances of 1.417(3) and 1.406(4) Å in the RuC_5H_5 ring of **1** are essentially equal and are consistent with a delocalized π-system. For comparison, the C−C distances in benzene are 1.397(1) Å[30] while the C−C distances in arene rings π-bonded to ruthenium centers fall in the range of 1.37−1.43 Å.[31−34] The C−C bond distances in **1** are slightly longer than those of known metallabenzene complexes in which the metallabenzene rings do not coordinate to a second metal,[9,11] but are comparable to those of metallabenzene rings that are η^6-bound to a second metal center.[14−17] It is well-known that when arenes complex to transition metal centers, the C−C bonds lengthen slightly and the ring aromaticity is reduced; these effects are attributed to the donation of arene π-electron density into vacant metal d-orbitals and some back-bonding into the arene δ^* orbital.[35,36]

Although the five carbon atoms in the RuC_5H_5 ring of **1** are coplanar (with the largest deviation from the least-squares plane being 0.01 Å), the sixth vertex Ru(1) is 0.32 Å out of the C_5H_5 plane. The dihedral angle between the C_{ortho}−Ru(1)−C_{ortho} unit and the C_5H_5 fragment is 13.0°.

Reaction of $[Cp^*RuCl_2]_2$ with Propadiene; Isolation of an Unusual Tetramethyleneethane Diruthenium Complex $Cp^*_2Ru_2(\eta^3{:}\eta^3\text{-}C_6H_8)Cl_4$, 4. Treatment of a slurry of $[Cp^*RuCl_2]_2$ in CH_2Cl_2 at −78 °C with propadiene gives a red solution from which golden brown crystals can be isolated after addition of diethyl ether. Elemental analysis and ^1H and ^{13}C NMR spectroscopy show the crystals to consist of an unusual tetramethyleneethane diruthenium complex $Cp^*_2Ru_2(\eta^3{:}\ \eta^3\text{-}C_6H_8)Cl_4$, **4**; the tetramethyleneethane group can also be thought of as a 2,2′-biallyl unit, a formulation which is more in keeping with its dianionic nature.



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The ^1H NMR spectrum of **4** contains two singlets at δ 3.90 and 2.28 for the *endo*- and *exo*-protons of the tetramethyleneethane groups, respectively. The resonance for the Cp* protons appears as a singlet at δ 1.61. The ^{13}C NMR spectrum of **4** shows a singlet at δ 105.9 and a doublet of doublets at δ 60.9 for the central and terminal carbons of the tetramethyleneethane group, respectively. The ^{13}C NMR spectrum of **4** also shows a singlet at δ 105.1 and a quartet at δ 9.5 for the quaternary and methyl carbons of the Cp* groups, respectively. As expected, these NMR spectroscopic data are very similar to those reported for the mononuclear ruthenium allyl complex $Cp^*Ru(\eta^3\text{-allyl})Br_2$.[37,38]

The tetramethyleneethane complex $Cp^*_2Ru_2(\eta^3{:}\ \eta^3\text{-}C_6H_8)Cl_4$ results from the coupling of two propadiene molecules. This behavior is not altogether surprising since the reactive $[Cp^*Ru^+]$ fragment has been shown to be able to promote carbon−carbon bond formation between other unsaturated hydrocarbons.[39,40] There have also been reports of the formation of tetramethyleneethane ligands from the reaction of propadiene with other organotransition metal complexes.[41−44] For example, the reaction of propadiene with either $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ affords the tetramethyleneethane complex $Fe_2(\eta^3{:}\ \eta^3\text{-}C_6H_8)(CO)_6$.[41−43] Similarly, the reaction of propadiene with Pd(acac)(allyl) affords the analogous palladium complex $Pd_2(\eta^3{:}\ \eta^3\text{-}C_6H_8)(acac)_2$ (where acac = acetylacetonate).[44]

Discussion

Folding of the Metallabenzene Ring in 1. In $Cp^*_2Ru_2(\eta^2{:}\eta^5\text{-}C_5H_5)(SiMe_3)$, the metal vertex Ru(1) is displaced 0.32 Å out of the C_5H_5 plane; thus, the metallabenzene ring is nonplanar. The ring is folded about a line that connects the two α-carbon atoms, and the dihedral angle described is 13.0°. The folding must be a consequence of the presence of the second ruthenium atom, since the metallabenzene rings in the mononuclear complexes $Os(\eta^3\text{-}CSC_4H_4)(CO)(PPh_3)_2$ and $Ir(\eta^2\text{-}C_5H_3Me_2)(PEt_3)_3$ are essentially planar.[9,11]

Salzer has proposed that the folding of the ring is directly correlated with the metal−metal bond length, with more planar rings being observed for shorter M−M bond lengths.[16] It is interesting to compare the parameters for **1** with those of other known dinuclear metallabenzene complexes (Table 3). Salzer's suggestion is not supported by these data; if anything, *longer* M−M distances are weakly correlated with smaller dihedral

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Table 3. Dihedral Angles Within the Metallabenzene Ring and Metal−Metal Bond Distances for Dinuclear Metallabenzene Complexes[a]

compound	ϕ_{dihedral} (deg)	$d_{\text{M-M}}$ (Å)	ref
$[Cp^*(MeCN)Ru(\eta^2{:}\eta^5\text{-}C_5H_3Me_2)RuCp^+]$	27.2	2.767	15
$[CpNi(\eta^2{:}\eta^5\text{-}C_5H_3Me_2)RuCp^{*+}]$	16.4	2.554	16
$Cp^*(SiMe_3)Ru(\eta^2{:}\eta^5\text{-}C_5H_5)RuCp^*$	13.0	2.898	this work
$(PEt_3)_3Ir(\eta^2{:}\eta^5\text{-}C_5H_3Me_2)Mo(CO)_3$	11.6	2.978	14
$(PEt_3)_2(PMe_3)Ir(\eta^2{:}\eta^5\text{-}C_5H_3Me_2)Mo(CO)_3$	9.5	2.950	14
$(\eta^5\text{-}C_5H_3Me_2)(CO)_2Mo(\eta^2{:}\eta^5\text{-}C_5H_3Me_2)Mo(CO)_3$	8.8	2.989	17
$[(PEt_3)_2(PMe_3)Ir(\eta^2{:}\eta^5\text{-}C_5H_3Me_2)(\mu\text{-}H)Mo(CO)_3{}^+]$	7.7	2.854	14

[a] The metal atom that is π-complexed to the ring is last in the formulas.

angles. Instead, the principal factor dictating the degree of ring folding appears to be steric repulsion between the ligands on the two metals:[15] as the steric repulsion increases, so does the degree of ring folding. More strongly folded rings will generally be seen when the metal−metal bond distance is short and when the ligands on each metal are large.

Aromaticity of the Metallabenzene Ring in 1. Metallabenzene complexes are still rare species,[12] and the aromaticity of such rings is of interest.[8] Even though the metallabenzene ring in **1** is π-complexed to a second metal center, it is possible that some aromaticity remains, just as it does for metal-complexed arene rings. Simple aromatic systems usually exhibit the following features: the ring is essentially planar, the C−C bond lengths are near 1.40 Å, and the C−C bonds do not alternate in a long/short pattern.[45] The structure of **1** clearly shows that these features are present.

One spectroscopic measure of aromaticity is the effect of the "ring current" on the ^{1}H and ^{13}C NMR chemical shifts.[46] The ^{1}H NMR chemical shift of the ortho protons in **1** is δ 9.75, which is deshielded relative to the ca. δ 7.3 shifts of normal aromatic protons. This deshielding of the ortho protons can be attributed to the magnetic anisotropy of the large heteroatom.[47,48] Similar deshielding effects have been observed for the ortho protons of heavy group 5 heterobenzenes; for example, the ortho protons of arsabenzene, stibabenzene, and bismabenzene appear at δ 9.68, 10.94, and 13.25, respectively.[47,48] More relevantly, the ortho proton resonances of all known metallabenzene complexes are also deshielded.[9−11,14−17]

In contrast, the meta and para protons of **1** are shielded relative to the shifts of normal aromatic protons, and they resonate at δ 4.94 and 4.32, respectively. This shielding is due to the complexation of the ruthenabenzene ring to the second ruthenium center, and similar shifts have been observed for arene rings (including other metallabenzene rings) upon coordination to a second transition metal center.[14−17] For example, Bleeke and co-workers have shown that the ortho and para protons of the iridabenzene ring in Ir(η^2-$C_5H_3Me_2$)(PEt_3)$_3$ are shifted significantly upfield (from δ 10.91 to 8.16 and from δ 7.18 to 6.31, respectively) upon π-complexation with a Mo(CO)$_3$ fragment.[14]

Additional information about the aromaticity of **1** can be derived from the $^1J_{\text{CH}}$ coupling constants, which average 153 Hz. These one-bond C−H coupling constants are in fact very close to that of benzene (159 Hz).[49] The $^1J_{\text{CH}}$ coupling constants in **1** are, however, somewhat smaller than the 175 Hz values for ruthenium π-complexes of simple arenes.[26,33]

Finally, we have noted above that the secondary isotope effects on the ^{13}C NMR chemical shifts seen upon replacing the ring hydrogens with deuterium are very similar to those reported for benzene.

Overall, the structural and NMR properties of **1** suggest that the metallabenzene ring has considerable aromatic character, but that the aromaticity is modified by the presence of both the σ- and π-bonded ruthenium centers in a way similar to that seen for heterobenzene complexes and for π-complexes of simple arenes.

Experimental Section

All operations were carried out under vacuum or under argon. Solvents were distilled under nitrogen from sodium benzophenone (pentane), sodium (toluene), or calcium hydride (dichloromethane) immediately before use. $[Cp^*RuCl_2]_2$ was prepared via literature methods.[50,51] $Cp^*_2Ru_2(\mu\text{-}CH_2)(SiMe_3)(\mu\text{-}Cl)$ was prepared as described previously.[22] Ethyne (Matheson) was purified by passage through a trap at −78 °C; this procedure removes the acetone which is present as a stabilizer. Ethyne-d_2 (Cambridge Isotopes) and propadiene (Linde) were used as received. IR spectra were recorded on a Perkin-Elmer 599B infrared spectrometer as Nujol mulls between KBr salt plates. The ^{1}H NMR data were obtained on a General Electric GN-500 spectrometer at 500 MHz, a General Electric QE-300 spectrometer at 300 MHz, or a General Electric NB-300 spectrometer at 300 MHz. The ^{13}C NMR data were obtained on a General Electric GN-500 spectrometer at 126 MHz or a General Electric NB-300 spectrometer at 75 MHz. The ^{2}H NMR data were obtained on a General Electric NB-300 spectrometer at 46 MHz. Chemical shifts are reported in δ units (positive shifts to high frequency) relative to TMS (^{1}H, ^{2}H, ^{13}C) or 85% H_3PO_4 (^{31}P). Microanalyses were performed by the University of Illinois Microanalytical Laboratory.

Reaction of $Cp^*_2Ru_2(\mu\text{-}CH_2)(SiMe_3)(\mu\text{-}Cl)$ with Ethyne: Synthesis of Bis(pentamethylcyclopentadienyl)($\eta^2{:}\eta^5$-penta-2,4-diene-1-yl-5-ylidene)(trimethylsilyl)diruthenium, $Cp^*_2Ru_2(\eta^2{:}\eta^5\text{-}C_5H_5)(SiMe_3)$, 1. A dark red solution of $Cp^*_2Ru_2(\mu\text{-}CH_2)(SiMe_3)(\mu\text{-}Cl)$ (0.287 g, 0.48 mmol) in toluene (50 mL) was transferred to a Fisher−Porter bottle and cooled to −78 °C. The bottle was then evacuated and filled with 1 atm of ethyne (free from acetone). The resulting mixture was warmed to 25 °C and stirred for 20 h. A dark red solution with some black precipitate was obtained. The solvent was removed under vacuum, and the residue was extracted with pentane (ca. 50 mL). The red pentane extract was filtered, and the filtrate was concentrated to ca. 5 mL and cooled to −25 °C to afford dark red crystals of the metallabenzene complex **1**. Yield: 0.058 g (20%). Anal. Calcd (found) for $C_{28}H_{44}Ru_2$-

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Si: C, 55.1 (55.8); H, 7.26 (7.50); Ru, 33.1 (29.8). Mp: 160 (dec). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 9.75 (dd, $^3J_{HH} = 6.0$ Hz, $^4J_{HH} = 1.0$ Hz, *o*-C*H*), 4.94 (dd, $^3J_{HH} = 7.0$ Hz, $^4J_{HH} = 6.0$ Hz, *m*-C*H*), 4.32 (tt, $^3J_{HH} = 7.0$ Hz, $^4J_{HH} = 1.0$ Hz, *p-CH*), 1.94 (s, C_5Me_5), 1.73 (s, C_5Me_5), −0.38 (s, $SiMe_3$). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 177.0 (dd, $^1J_{CH} = 140$ Hz, $^2J_{CH} = 7$ Hz, *o-CH*), 97.6 (s, C_5Me_5), 90.1 (s, C_5Me_5), 86.8 (dd, $^1J_{CH} = 156$ Hz, $^2J_{CH} = 6$ Hz, *m*-*C*H), 83.4 (d, $^1J_{CH} = 164$ Hz, *p*-*C*H), 11.8 (q, $^1J_{CH} = 127$, C_5Me_5), 11.2 (q, $^1J_{CH} = 126$ Hz, C_5Me_5), 11.0 (q, $^1J_{CH} = 118$ Hz, $SiMe_3$). IR (cm^{-1}): 1289 (m), 1240 (m), 1226 (m), 1153 (vw), 1065 (w), 1020 (s), 962 (w), 914 (w), 830 (vs), 806 (m), 731 (m), 642 (m), 605 (m), 591 (m), 501 (vw), 420 (w).

The known arene complex $[Cp^*Ru(\eta^6\text{-}C_6H_6)]Cl$, **2**, and the known bridging metallacyclopentadiene complex $Cp^*_2Ru_2(\eta^2{:}\eta^4\text{-}C_4H_4)Cl_2$, **3**, were also isolated from this reaction. Addition of small amounts of Et_2O to the CH_2Cl_2 extract of the reaction mixture immediately induced precipitation of orange-red $[Cp^*Ru(\eta^6\text{-}C_6H_6)]Cl$, **2**. Cooling of the CH_2Cl_2/Et_2O filtrate to −20 °C afforded red crystals of $Cp^*_2Ru_2(\eta^2{:}\eta^4\text{-}C_4H_4)Cl_2$, **3**.

Analytical and NMR Data for 2. Anal. Calcd (found) for $C_{16}H_{21}ClRu$: C, 54.9 (53.6); H, 6.05 (6.16); Cl, 10.1 (10.4). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 5.92 (s, 6H, C_6H_6), 2.02 (s, 15H, C_5Me_5). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ 97.2 (s, C_5Me_5), 87.6 (s, C_6H_6), 10.9 (s, C_5Me_5).

Analytical and NMR Data for $3\cdot{}^1/_2CH_2Cl_2$. Anal. Calcd (found) for $C_{24.5}H_{35}Cl_3Ru_2$: C, 44.1 (44.3); H, 5.33 (5.57); Cl, 20.8 (19.5), 28.2 (29.7); ^{1}H NMR (CD_2Cl_2, 25 °C): δ 8.25 (t, $^3J_{HH} = {}^4J_{HH} = 2.5$ Hz, 2H, C_4H_4), 5.39 (t, $^3J_{HH} = {}^4J_{HH} = 2.5$ Hz, 2H, C_4H_4), 1.78 (s, 15H, C_5Me_5), 1.25 (s, 15 H, C_5Me_5). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 164.3 (dd, $^1J_{CH} = 174$ Hz, $^2J_{CH} = 13$ Hz, C_4H_4), 104.9 (s, C_5Me_5), 94.7 (dq, $^1J_{CH} = 166$ Hz, $^2J_{CH} = {}^3J_{CH} = 6$ Hz, C_4H_4), 94.4 (s, C_5Me_5), 10.9 (q, $^1J_{CH} = 127$ Hz, C_5Me_5), 9.8 (q, $^1J_{CH} = 127$ Hz, C_5Me_5).

Reaction of $Cp^*_2Ru_2(\mu\text{-}CH_2)(SiMe_3)(\mu\text{-}Cl)$ with Ethyne-d_2: Synthesis of $Cp^*_2Ru_2(\eta^2{:}\eta^5\text{-}C_5HD_4)(SiMe_3)$, 1-$d_4$. The reaction of $Cp^*_2Ru_2(\mu\text{-}CH_2)(SiMe_3)(\mu\text{-}Cl)$ with ethyne-d_2 was carried out exactly in the same way as above, except ethyne-d_2 was used in place of ethyne. ^{1}H, ^{2}H, and ^{13}C NMR spectra showed that the metallabenzene complex obtained in this way retains one proton in one of the ortho positions of the ruthenabenzene ring. ^{1}H NMR (CD_2Cl_2, 25 °C): δ 9.74 (s, *o-CH*), 1.94 (s, C_5Me_5), 1.72 (s, C_5Me_5), −0.38 (s, $SiMe_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 25 °C): δ 176.8 (s, *o*-*C*H), 176.4 (t, $^1J_{CD}$ = 22 Hz, *o*-*C*D), 97.6 (s, C_5Me_5), 90.0 (s, C_5Me_5), 86.3 (td, $^1J_{CD} = 24$ Hz, $^2J_{CH} = 6$ Hz, *m*-*C*D), 83.0 (t, $^1J_{CD} = 24$ Hz, *p*-*C*D), 11.3 (s, C_5Me_5), 11.2 (s, C_5Me_5), 11.0 (s, $SiMe_3$).

Bis(pentamethylcyclopentadienyl)(μ,$\eta^3{:}\eta^3$-2,3-dimethylenebuta-1,4-diyl)tetrachlorodiruthenium, $Cp^*_2Ru_2(\mu,\eta^3{:}\eta^3\text{-}C_6H_8)Cl_4$, 4. A Fisher−Potter bottle charged with a cold (−78 °C) slurry of $[Cp^*RuCl_2]_2$ (0.57 g, 0.93 mmol) in CH_2Cl_2 (30 mL) was first evacuated and then charged with propadiene (5.0 mmol). The resulting mixture was then warmed to room temperature. After the mixture had been stirred for 3 h, the dark red solution was filtered, concentrated to ca. 3 mL, and treated with diethyl ether (ca. 2 mL). The resulting mixture was cooled to −20 °C to afford red crystals. Yield: 0.22 g (34%). Mp: 170 °C (dec). Anal. Calcd (found) for $C_{32}H_{38}Ru_2Cl_4$: C, 45.0 (45.5); H, 5.51 (5.63); Cl, 20.4 (21.3); Ru, 29.1 (27.3). ^{1}H NMR (CD_2Cl_2, 500 MHz, 25 °C): δ 3.90 (s, CH_2), 2.28 (s, CH_2), 1.61 (s, C_5Me_5). ^{13}C NMR (CD_2Cl_2, 126 MHz, 25 °C): δ 105.9 (s, CCH_2), 105.1 (s, C_5Me_5), 60.9 (t, $^1J_{CH}$ = 163 Hz, CCH_2), 9.5 (q, $^1J_{CH} = 130$ Hz, C_5Me_5). IR (cm^{-1}): 1070 (w), 1010 (s), 936 (vw), 793 (vw), 610 (vw), 593 (m), 403 (vw), 384 (m).

Crystallographic Studies.[52] Single crystals of $Cp^*_2Ru_2(\eta^2{:}\eta^5\text{-}C_5H_5)(SiMe_3)$, **1**, grown from pentane, were mounted on glass fibers using Paratone-N oil (Exxon) and were immediately cooled to −75 °C in a nitrogen stream on the diffractometer. Standard peak search and indexing procedures gave rough cell dimensions, and the crystal symmetry was supported by examinations of the diffraction pattern. Least squares refinement using 25 reflections yielded the cell dimensions given in Table 1.

Data were collected in one octant ($+h$, $-k$, $-l$), and limited data between 4° and 14° in 2θ were collected in all eight octants to verify the crystal symmetry. The systematic absences $0kl$ ($k + l \neq 2n$) and $hk0$ ($h \neq 2n$) were consistent with the space groups *Pnma* and $Pna2_1$. The centric choice *Pnma* was subsequently confirmed by successful solution and refinement of the proposed model. The measured intensities were reduced to structure factor amplitudes and their esd's by correction for background, scan speed, and Lorentz and polarization effects. While corrections for crystal decay were unnecessary, absorption corrections were applied. The maximum and minimum transmission factors were 0.794 and 0.580, respectively. Systematically absent reflections were deleted, and symmetry equivalent reflections were averaged to yield the set of unique data. Only those data with $I > 2.58\ \sigma(I)$ were used in the least-squares refinement.

The structure was solved by direct methods (SHELXS-86) and unweighted difference Fourier syntheses. The ruthenium and silicon atoms were found from an *E*-map. Mirror symmetry normal to the *b*-axis was imposed on the molecular model. Subsequent least-squares refinement and difference Fourier synthesis revealed the positions of the all remaining atoms. The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)^2$, where $w = 2.54/(\sigma(F_o)^2 + (pF_o)^2)$. The analytical approximations to the scattering factors were used, and all structure factors were corrected for both the real and imaginary components of anomalous dispersion. In the final cycle of least squares, all atom positions were independently refined. The non-hydrogen atoms were refined with anisotropic thermal coefficients, and the hydrogen atoms were refined with independent isotropic thermal parameters. An empirical isotropic extinction parameter was also refined, which converged to $1.8(2) \times 10^{-8}$. Successful convergence was indicated by the maximum shift/error of 0.061 in the last cycle. Final refinement parameters are given in Table 1. The largest peaks in the final difference Fourier map were in the vicinity of the ruthenium atom. A final analysis of variance between observed and calculated structure factors showed no systematic errors.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE 89-21757) for support of this work and Teresa Prussak-Wieckowska for assistance with the X-ray crystallographic determination. W.L. acknowledges receipt of a University of Illinois Department of Chemistry Fellowship.

Supporting Information Available: Tables of all crystal data, atomic coordinates, displacement parameters, and bond distances and angles for **1** (8 pages). Ordering information is given on any current masthead page.

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[52] For a description of the crystallographic methods and programs employed, see: Jensen, J. A.; Wilson, S. R.; Girolami, G. S. *J. Am. Chem. Soc.* **1988**, *110*, 4977−4982.