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Comparative Study of the Reactivity of $(Cp^*RuCl)_4$ and $(Cp^*RuCl_2)_2$ with Silylated Dienyl Ligands[⊥]

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Reaction of the well-known precursors $[Cp^*RuCl]_4$ (**1**) and $[Cp^*RuCl_2]_2$ (**2**) with the silyl-diene compound $CH_2{=}CHCH{=}CHCH_2SiMe_3$ (**3**), in THF, results in the selective formation of $[Cp^*Ru(\eta^4\text{-}CH_2CHCHCHCH_2SiMe_3)Cl]$ (**4**) from the diamagnetic tetramer **1**, while the reaction of dimer **2** leads to nonselective reactions with the formation of **4**, $[Cp^*Ru(\eta^3\text{-}CH_2CHCHCHCH_2)Cl_2]$ (**5**), and $[Cp^*Ru(\eta^3\text{-}CH_2CHCHCHCHSiMe_3)Cl_2]$ (**6**). Reaction of **2** with **3**, in ethanolic solution at room temperature, provided a preparative route to the corresponding diene **4** and the allyl ruthenium(IV) complex **5**. Compound **4**, in the presence of chloroform, affords **6**, and recrystallization of **5** with CH_2Cl_2/hexane affords $[Cp^*Ru(\eta^3\text{-}CH_2CHCHEt)Cl_2]$ (**7**), but contrastingly, the manipulation of compound **5** in plates of silica gel affords $[Cp^*Ru(\eta^4\text{-}CH_2CHCHCHCH_2OH)Cl]$ (**8**). A $CDCl_3$ or C_6D_6 solution of **8** in the presence of traces of oxygen affords $Cp^*Ru(\eta^4\text{-}CH_2CHCHCHCHO)Cl$ (**9**), which slowly decomposes to liberate 2,4-pentadienal in the reaction media, along with unknown Cp*Ru species. A comparative study is established between the chemical reactivity of **1** and **2** toward the trimethylsilylpentadiene and the corresponding analogous trimethylsilyl-substituted dienyloxy ligands. Some representative crystalline structures of compounds **4**, **6**, and **8** were determined by X-ray crystallography.

Introduction

Previous studies of the precursors $[Cp^*RuCl]_4$ $(\mathbf{1})^{1-4}$ and $[Cp^*RuCl_2]_2$ $(\mathbf{2})^{3-6}$ have been established for silylated dienyloxy ligands,[4] such as $CH_2CHCHCHOSiMe_3$ and the mixture of methyl-substituted isomers $CH_2C(Me)CHC(OSiMe_3)Me$ and $MeC(Me)CHC(OSiMe_3)CH_2$, and in fact, it has been observed that most of the reactions with these ligands have led to loss of the $SiMe_3$ fragment through cleavage of the O−Si bond.[7−10] The siloxy substituents have been proven to be quite useful for organic transformations[11] and not as stable as their silyl analogues.[12] There are just a few examples of silyl-containing pentadienyl species with transition metals, such as $CpM[1,5\text{-}(Me_3Si)_2C_5H_5]$ (M = V, Cr),[13] $M[1,5\text{-}(Me_3Si)_2C_5H_5]_2$ (M = Ti, Zr),[14] and $K[Mn\{3\text{-}Me\text{-}1,5\text{-}(Me_3Si)_2C_5H_4\}_3]$,[15] as well as the $[(4\text{-triethylsilyl-1-methyl-}\eta^5\text{-pentadienyl})Fe(CO)_3]PF_6$,[16a] $[(3\text{-trimethylsilyl-2,4-cyclohexadienylium})Fe(CO)_3]PF_6$,[16b] $[(3\text{-trimethylsilylcycloheptadienyl})Fe\text{-}(CO)_3]^+$,[16c] and trimethylsilyl-substituted(cyclohexadiene)$Fe(CO)_3$ compounds,[16b,d,e] $[(3\text{-trimethylsilylcyclohexadienyl})Fe(CO)_3]$ cations,[16b,e] and quite

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[⊥] Dedicated to Professor Heinrich Nöth, friend and colleague, on the occasion of his 80th birthday and in recognition of his seminal contributions in chemistry.

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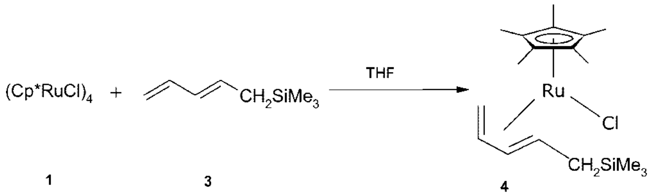
Scheme 1



recently, the [CpZr(I$_2$)(η^5-3-trimethylsilyl-6,6-dimethylcyclohexadienyl],[17] [bis(3-trimethylsilyl-6,6-dimethylcyclohexadienyl)Fe],[18] and silapentadienyl iridium phosphine complexes.[19] Also, only a few trimethylsiloxybutadiene ligands have been described in the literature, appearing in molybdenum,[9a,b,10] palladium,[9c] and ruthenium coordination spheres.[2f,4,7]

In our hands Cp*RuCl(η^4-CH$_2$CHCHCHOSiMe$_3$), obtained from the reaction of **1** or **2** and trimethylsiloxybutadiene in THF, was found to disproportionate to Cp*RuCl(η^5-CH$_2$CHCHCHO) and Cp*Ru(Cl)$_2$(η^3-CH$_2$CHCHCHO).[4,7]

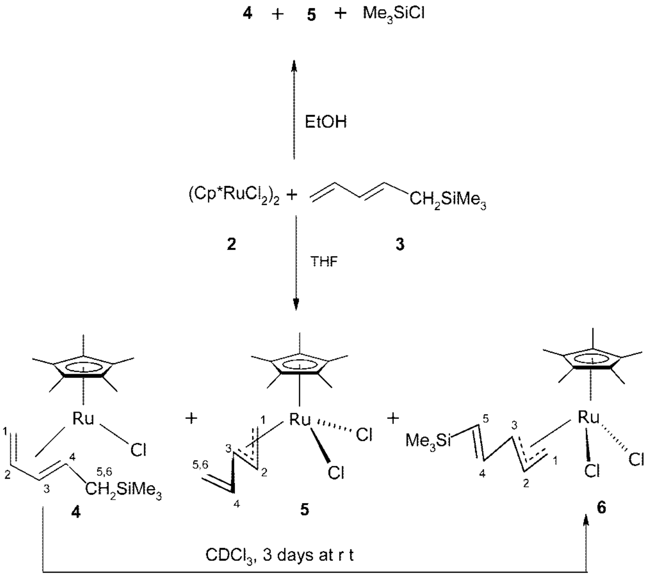
As far as we know, there are no silyl-diene ruthenium compounds reported until now, and thus it was of interest to establish a comparative study of the hydrocarbon analogue trimethylsilylpentadiene with the corresponding trimethylsiloxybutadiene[4,7] in the presence of **1** and **2**. The new silyl, allyl, and diene compounds derived from this study are discussed and compared with corresponding siloxy-diene, siloxy-dienyl, and oxodienyl derivatives.

Results

Reactivity of (Cp*RuCl)$_4$ (1) and (Cp*RuCl$_2$)$_2$ (2) toward Trimethylsilylpentadiene (3). (a) Reactions in THF. The [Cp*Ru(η^4-CH$_2$CHCHCHCH$_2$SiMe$_3$)Cl] complex (**4**) was formed cleanly at −110 °C and subsequently isolated in 50% yield as an orange-red crystalline solid, from the reaction of trimethylsilylpentadiene CH$_2$=CHCH=CHCH$_2$SiMe$_3$ (**3**) with (Cp*RuCl)$_4$ (**1**), Scheme 1.

The complex is stable in the solid state and decomposes slowly on exposure to air. It is soluble in hexane, diethyl ether, benzene, and chlorinated solvents. ^{1}H and ^{13}C NMR spectroscopy showed that compound **4** exhibits an acyclic 1−4-η-*cis*-diene ligand coordination to the metal center, as well as the expected η^5-Cp* ligand. The chemical shifts were typical of those found for dienes coordinated to ruthenium,[1b,2d,e,6a,20] and the presence of the SiMe$_3$ group was confirmed by ^{29}Si NMR spectroscopy.

Scheme 2



Compound **4** can be purified by chromatography using either silica gel or alumina without suffering disproportionation, contrasting with the corresponding analogous siloxy-diene derivative [Cp*Ru(η^4-CH$_2$CHCHCHOSiMe$_3$)Cl] (*vide supra*).[4,7] The different reactivity is attributed to the different polarity between O−Si and C−Si bonds.

In contrast to the results described in Scheme 1, the reaction of (Cp*RuCl$_2$)$_2$ (**2**) with **3**, at room temperature, led to nonselective reactions with the formation of three compounds: **4**, [Cp*Ru(η^3-CH$_2$CHCHCHCH$_2$)Cl$_2$] (**5**), and [Cp*Ru(η^3-CH$_2$CHCHCHCHSiMe$_3$)Cl$_2$] (**6**), in a 0.4:0.3:1.0 ratio, respectively, Scheme 2.

The mixture of compounds **4**, **5**, and **6** could be purified by solvent extractions, followed by silica gel column chromatography. Complexes **4** and **6** were extracted with hexane and separated on a silica gel column using diethyl ether as eluent, obtaining 20−25% and 20% yields, respectively, while compound **5** was obtained, in traces, from a chromatographic separation of **5** and **6** using ethyl acetate and diethyl ether, respectively. However, the isolation of **5** is facilitated if ethanol is used as a solvent in the reaction of **2** and **3** (*vide infra*). A slightly better yield of **6** can be reached by exposure of **4** to chloroform, *vide infra*, Scheme 2.

The same preferential η^3-*endo*-*syn* orientation of the acyclic ligand was observed for compounds **5** and **6**, according to their $^3J_{H2-H3}$ values of 10.3 and 10.1 Hz, respectively. The same conformation was observed, in the solid state and in solution, for [Cp*Ru(η^3-CH$_2$CHCHCHO)Cl$_2$].[4,7]

The ^{13}C NMR spectra showed the characteristic vinylic carbons C$_4$ (δ 138.8) and C$_5$ (δ 120.5) for **5** and internal double-bond atoms C$_4$ (δ 145.5) and C$_5$ (δ 140.8) for **6**. Typical chemical shifts for the corresponding allylic carbon atoms of **5** and **6** were observed in the range δ 64−96.

(b) Reaction in EtOH. A stoichiometric reaction of compound **2** and ligand **3** in EtOH after 4 h at room temperature afforded compounds **4** and **5** in a 1:1 ratio. Compounds **4** and **5** were extracted from hexane and methylene chloride in 30% and 47% yields, respectively. The formation of compound **4** in EtOH suggests that a more reductive reaction mixture is present in this case compared to the dienyloxy analogues, for which oxidative addition affords [Cp*Ru(η^3-CH$_2$CHCHCHO)Cl$_2$].[4]

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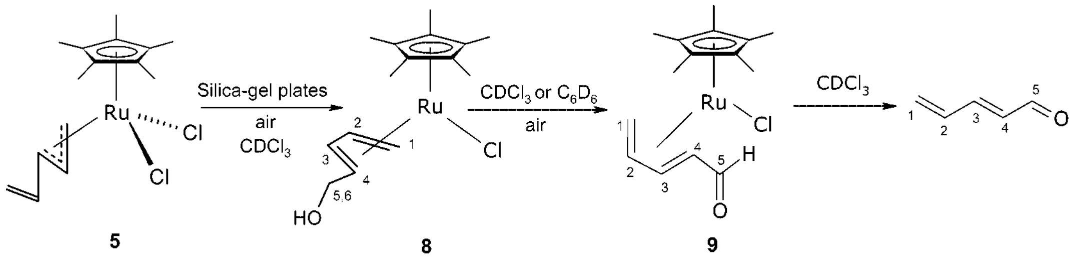
Scheme 3



Compound **5** was formed directly from **2** and the trimethylsilyl-substituted pentadiene ligand **3**, through C−Si bond cleavage and formation of Me_3SiCl; contrastingly, its analogous oxodienyl compound [Cp*Ru(η^3-$CH_2CHCHCHO$)Cl_2][4,7] has been formed, along with Cp*Ru(η^5-$CH_2CHCHCHO$), from the disproportionation reaction of the η^4-diene-coordinated compound [Cp*Ru(η^4-$CH_2CHCHCHOSiMe_3$)Cl][4,7](*vide supra*).

This fact was confirmed when a chloroform solution of **4** afforded [Cp*Ru(η^3-$CH_2CHCHCHCHSiMe_3$)Cl_2] (**6**) (Scheme 2), as a result of the C−H activation of the methylene group and concomitant retention of the trimethylsilyl fragment in the newly formed molecule. The abstraction of hydrogen atoms α to silicon has been achieved in the presence of TMEDA or LDA, and under these conditions it has been observed that the $SiMe_3$ group is untouched.[11] In this case, the activation of a C−H bond of the CH_2 group was favored due to the generation of carbenes from the chloroform, leading to the presence of methylene chloride, which was clearly observed during the monitoring of the reaction through ^1H NMR spectroscopic techniques.

A comparison between the oxodienyl complex [Cp*Ru(η^4-$CH_2CHCHCHOSiMe_3$)Cl] and the corresponding hydrocarbon analogue **4** has shown that both compounds are quite stable, as pure samples, under an inert atmosphere. However, the isolation and purification of the orange-red compound **4** was significantly more complicated because it decomposes easily, even from traces of some impurities. The corresponding comparison between compounds [Cp*Ru(η^3-$CH_2CHCHCHO$)Cl_2] and **5** showed that **5** was not as stable as the oxodienyl analogue because it could easily undergo transformation in solution or under chromatographic conditions. Also, compound **6** was substantially more stable in the presence of oxygen or chlorinated solvents than **5**. But, without a doubt, the highest stability for these Ru(IV) compounds is observed for the oxodienyl [Cp*Ru(η^3-$CH_2CHCHCHO$)Cl_2]. The allylic complex [Cp*Ru(η^3-$CH_2CHCHCH_2CH_3$)Cl_2] (**7**) could also be isolated on the recrystallization of **5** with CH_2Cl_2/hexane. It should be mentioned that the formation of **7** requires the hydrogenation of the C=C bond, and it is only formed during the process of purification of compound **5**. Compound **7** shows the enyl-coordinated ligand in an *endo*-conformation.

Manipulation of compound **5** on silica gel plates afforded two fractions, which were orange and green. The last fraction contained green paramagnetic species, which were not fully characterized, but were tentatively assigned as mixed-valence ruthenium complexes with bridging halogens such as the green complex Ru(II)/(III) [Cp*Ru(μ_2-Cl)$_3$RuCp*] previously observed by Koelle.[5e] The orange fraction afforded an orange-red powder of [Cp*Ru(η^4-$CH_2CHCHCHCH_2OH$)Cl] (**8**) in 30% yield (Scheme 3). ^1H NMR spectra of **8**, in C_6D_6, showed chemical shifts of the butadiene fragment to low frequency, which suggest coordination to the ruthenium center; the hydrogen atom of the OH group appeared as a doublet of doublets (J = 2.4, 5.8 Hz) due to coupling with the diastereotopic CH_2 hydrogens. Exchange with D_2O confirmed the assignment, as well as the infrared spectrum, which showed an absorption band at 3465 cm^{-1}, characteristic of the OH group.

A C_6D_6 solution of **8** in the absence of air is quite stable, whereas after 15 days in the presence of traces of oxygen, [Cp*Ru(η^4-$CH_2CHCHCHCHO$)Cl] (**9**) is formed. The oxidation of the noncoordinated double bond in the pentadienyl ligand of compound **5** affords the alcohol derivative **8**, which in the presence of air was transformed to the corresponding aldehyde **9**.

These reactions could occur by activation of molecular oxygen from the air, as it has been observed for the oxidation of alkenes in the presence of oxygen.[21] However, if $CDCl_3$ was used instead of C_6D_6, the transformation occurred in 5 days, and it was possible to observe the formation of 2,4-pentadienal, as well as the corresponding intermediate **9** (Scheme 3). This sort of transformation, assisted by chlorinated solvents, has been observed in terminal alkene oxidations based on dichlororuthenium(IV)-porphyrin catalysts in chlorinated solvents, such as $CHCl_3$ or CH_2Cl_2, which produced aldehydes in quantitative yields.[21a]

Compound **9** has been characterized only by ^1H and ^{13}C NMR spectroscopy. It showed, in $CDCl_3$, a *cis*-coordinated butadiene ligand as revealed by $^3J_{H2,H3}$ = 5.8 Hz and the broad doublet for the aldehyde hydrogen ($^3J_{H4,H5}$ = 1.6 Hz), Table 1. After 11 days, only the free aldehyde was observed, along with a Cp*Ru signal at 1.60 ppm, which was not assigned to a specific compound. After 15 days, compound **5** in $CDCl_3$ showed complete transformation to 2,4-pentadienal,[22] along with Cp*Ru species lacking coordinated pentadienyl ligands.

From the above it is clear that different chemistry is involved in **5** as compared to its oxodienyl analogues due to the presence of the terminal C=C bond instead of the carbonyl group in the corresponding oxodienyl derivative.[4] The uncoordinated double bond in compound **5** leads to a much more reactive system, once it can be hydrogenated and oxidized to afford compound **7** and functionalized dienes, such as Ru(II) alcohol (**8**) and aldehyde (**9**) derivatives, respectively. Complex **9** could also afford the free α,*β*,*γ*-unsaturated ligand, which could be interesting to study with a variety of transition metals.

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Table 1. ^{1}H NMR Data[a] for Compounds 4−9

compound	H_{1a}	H_{1s}	H_2	H_3	H_4	H_5	H_6 or Me_6	$SiMe_3$ or OH	Cp*
4	1.38 (d) $J_{H1a,H2} = 10.4$	3.02 (dd) $J_{H1a,H1s} = 1.6$ $J_{H1s,H2} = 7.6$	4.25 (m)	4.43 (dd) $J_{H2,H3} = 5.6$ $J_{H3,H4} = 10.8$	2.40 (td) $J_{H4,H5} = 11.3$ $J_{H3,H4} = 11.3$ $J_{H4,H6} = 3.8$	1.05 (dd) $J_{H4,H5} = 11.6$ $J_{H5,H6} = 13.4$	1.36 (dd) $J_{H4,H6} = 3.8$ $J_{H5,H6} = 13.5$	0.03 (s)	1.62 (s)
4[b]	1.82 (dd) $J_{H1a,H1s} = 1.9$ $J_{H1a,H2} = 10.4$	2.94 (dd) $J_{H1a,H1s} = 1.8$ $J_{H1s,H2} = 7.5$	3.86 (ddd) $J_{H1a,H2} = 10.0$ $J_{H1s,H2}$ 6.8 $J_{H2,H3} = 5.3$	4.20 (dd) $J_{H2,H3} = 5.3$ $J_{H3,H4} = 10.6$	2.71 (ddd) $J_{H4,H5} = 14.8$ $J_{H3,H4} = 11.1$ $J_{H4,H6} = 3.8$	1.05 (dd) $J_{H4,H5} = 11.6$ $J_{H5,H6} = 13.3$	1.58 (dd) $J_{H4,H6} = 3.8$ $J_{H5,H6} = 13.4$	0.46 (s)	1.34 (s)
5	2.33 (d) $J_{H1a,H2} = 9.6$	4.22 (d) $J_{H1s,H2} = 6.0$	5.40 (ddd) $J_{H1a,H2} = 9.8$ $J_{H1s,H2} = 6.1$ $J_{H2,H3} = 10.0$	3.25 (t) $J_{H2,H3} = 10.3$ $J_{H3,H4} = 10.3$	6.62 (ddd) $J_{H4,H5} = 17.1$ $J_{H3,H4} = 10.3$ $J_{H4,H6} = 10.3$	5.31 (dd) $J_{H4,H5} = 17.1$ $J_{H5,H6} = 1.4$	5.61 (dd) $J_{H4,H6} = 10.1$ $J_{H5,H6} = 1.4$		1.58 (s)
5[b]	1.67 (d) $J_{H1a,H2} = 9.4$	4.17 (d) $J_{H1s,H2} = 6.0$	5.46 (m)	2.67 (t) $J_{H2,H3} = 10.3$ $J_{H3,H4} = 10.3$	6.86 (m)	4.90 (d) $J_{H4,H5} = 18.8$	5.32 (d) $J_{H4,H6} = 10.3$		1.03 (s)
6	2.28 (d) $J_{H1a,H2} = 9.9$	4.17 (d) $J_{H1s,H2} = 6.2$	5.39 (ddd) $J_{H1a,H2} = 9.7$ $J_{H1s,H2} = 6.2$ $J_{H2,H3} = 9.8$	3.25 (t) $J_{H2,H3} = 10.1$ $J_{H3,H4} = 10.1$	6.80 (dd) $J_{H3,H4} = 10.2$ $J_{H4,H5} = 18.4$	5.99 (d) $J_{H4,H5} = 18.5$		0.09 (s)	1.55 (s)
6[b]	2.69 (d) $J_{H1a,H2} = 9.4$	4.17 (d) $J_{H1s,H2} = 6.1$	5.54 (ddd) $J_{H1a,H2} = 9.8$ $J_{H1s,H2} = 6.0$ $J_{H2,H3} = 9.8$	2.77 (t) $J_{H2,H3} = 9.8$ $J_{H3,H4} = 9.8$	7.16[c]	5.81 (d) $J_{H4,H5}$ =18.5		0.20 (s)	1.01 (s)
7	2.29 (d) $J_{H1a,H2} = 9.5$	4.12 (d) $J_{H1s,H2} = 6.0$	5.03 (ddd) $J_{H1a,H2} = 9.2$ $J_{H1s,H2} = 6.1$ $J_{H2,H3} = 9.8$	2.93 (td) $J_{H3,H2} = 9.9$ $J_{H3,H4} = 3.5$ $J_{H3,H5} = 3.5$	2.19 (m)	1.59[d]	1.14 (t) $J_{H5,H6} = 7.5$		1.59 (s)
8	1.49 (dd) $J_{H1a,H1s} = 1.8$ $J_{H1a,H2} = 10.6$	3.00 (dd) $J_{H1a,H1s} = 1.8$ $J_{H1s,H2} = 7.5$	4.35 (ddd) $J_{H1a,H2} = 10.3$ $J_{H1s,H2} = 7.7$ $J_{H2,H3} = 5.1$	4.66 (dd) $J_{H2,H3} = 5.1$ $J_{H3,H4} = 9.7$	2.27 (td) $J_{H4,H5} = 4.4$ $J_{H3,H4} = 9.9$ $J_{H4,H6} = 9.8$	4.18 (m)	3.58 (m)	2.49 (dd) OH $J_{H6,H(OH)} = 2.9$ $J_{H5,H(OH)} = 6.6$	1.68 (s)
8[b]	1.68 (dd) $J_{H1a,H1s} = 1.8$ $J_{H1a,H2} = 10.5$	2.86 (dd) $J_{H1a,H1s} = 1.9$ $J_{H1s,H2} = 7.5$	3.71 (ddd) $J_{H1a,H2} = 10.4$ $J_{H1s,H2} = 7.5$ $J_{H2,H3} = 5.2$	4.04 (dd) $J_{H2,H3} = 5.2$ $J_{H3,H4} = 9.6$	2.50 (td) $J_{H4,H5} = 4.2$ $J_{H3,H4} = 9.9$ $J_{H4,H6} = 9.8$	4.25 (m)	3.45 (dt) $J_{H6,H(OH)} = 2.4$ $J_{H5,H6} = 9.6$ $J_{H4,H6} = 9.6$	3.10 (dt)OH $J_{H6,H(OH)} = 2.4$ $J_{H5,H(OH)} = 5.8$	1.28 (s)
9	2.00 (d) $J_{H1a,H2} = 11.5$	3.45 (d) $J_{H1s,H2} = 8.2$	4.62 (m)	5.24 (dd) $J_{H2,H3} = 5.8$ $J_{H3,H4} = 9.5$	2.53 (dd) $J_{H3,H4} = 9.8$ $J_{H4,H5} = 1.6$	9.48 (d,br) $J_{H4,H5} = 1.6$			1.59 (s)
9[b]	2.12 (dd) $J_{H1a,H1s} = 1.9$ $J_{H1a,H2} = 10.9$	3.12 (dd) $J_{H1a,H1s} = 2.1$ $J_{H1s,H2} = 7.6$	3.85 (m)	4.95 (dd) $J_{H2,H3} = 5.4$ $J_{H3,H4} = 9.4$	2.14 (d) $J_{H3,H4} = 9.5$	9.56 (s,br)			1.28 (s)

[a] δ (ppm), $CDCl_3$. For numbering see Schemes 2 and 3. [b] C_6D_6. [c] Overlaps solvent signal. [d] Overlaps Cp* signal.

Structural Studies

The structures of compounds **4**, **6**, and **8** were confirmed through single-crystal X-ray diffraction studies. Crystal data for these ruthenium compounds are provided in Table 2.

η^4-Butadiene Compounds [Cp*Ru(η^4-$CH_2CHCHCHCH_2SiMe_3$)Cl] (4) and [Cp*Ru(η^4-$CH_2CHCHCHCH_2OH$)Cl] (8). Molecular structures **4** and **8** are presented in Figures 1 and 2; some relevant bond distances and angles are provided in Table 3.

Complex **4** was obtained from hexane at −5 °C. The crystal structure determination revealed the presence of two independent molecules in the unit cell. These molecules are structurally identical, and for clarity only one is shown in Figure 1. Compound **8** crystallized as orange-red crystals from diffusion of CH_2Cl_2 and hexane solutions at −5 °C. Both structures have their butadiene fragment bound in an η^4-*cis* fashion to the ruthenium atom with an *exo*-conformation, having the two CH_2 and CH groups pointing to the chloride ligand, which is characteristic for related ruthenium(II) compounds.[1b,23] The butadiene centroid−Ru distances are 1.799 and 1.787 Å for **4** and **8**, respectively, and the corresponding centroid Cp*−Ru distances for **4** (1.855 Å) and **8** (1.851 Å) are longer, as expected. The dihedral angle between the Cp* and the diene planes is 21.17° for **4**, which is smaller than the value of 33.2° for [Cp*Ru(η^4-$CH_2CHCHCH_2$)I][1b] and similar to those of [Cp*Ru(η^4-$CH_2CHCHCH_2$)OSO_2CF_3] (20.2°) and [Cp*Ru(η^4-$CH_2CHCHCH_2$)$OCOCF_3$] (19.7°).[23a]

The C−C bonds of the diene fragment in compound **4** exhibited a short−long−short pattern C1−C2 1.390(5), C2−C3 1.431(5), and C3−C4 1.387(4) Å. The Ru−C bond distances were long for C1 and C4 [2.204(3) and 2.282(3) Å] and short for C2 and C3 [2.156(3) and 2.190(3) Å], respectively, which are characteristic of a diene that is predominantly π-bound to a transition metal.[23a]

In comparison, the butadiene fragment of compound **8** exhibited a similar pattern in bond distances between ruthenium and the diene [Ru−C1, 2.207(6), Ru−C4, 2.225(5), Ru−C2, 2.167(5), and Ru−C3, 2.159(5) Å], but a different trend in C−C bond distances for the coordinated diene: C1−C2 1.429(10), C2−C3 1.403(10), and C3−C4 1.379(8) Å.

η^3-Allyl Compound [Cp*Ru(η^3-$CH_2CHCHCHCHSiMe_3$)Cl_2] (6). Crystals for **6** were obtained from $CHCl_3$/hexane at −5 °C, and one molecule of $CHCl_3$ cocrystallized with compound **6**. The molecular structure for **6** is depicted in Figure 3. Selected bond distances and angles are listed in Table 4.

The enyl moiety in **6** is asymmetrically bonded to the metal in an *endo*-conformation (Figure 3), with Ru−C terminal distances of 2.186(4) and 2.301(4) Å for Ru1−C1 and Ru1−C3, respectively, while the internal Ru1−C2 bond [2.141(4) Å] is the shortest, as observed in many *endo*-allyl complexes. The C−C bond distances within the enyl ligand are similar [C1−C2

Table 2. Crystal Data for Ruthenium Compounds 4, 6, and 8

	4	**6**	**8**
formula	$C_{18}H_{31}ClRuSi$	$C_{18}H_{30}Cl_2RuSi \cdot CHCl_3$	$C_{15}H_{23}ClORu$
fw	412.04	565.87	355.85
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/n$	*Pbca*	$P2_1/n$
a (Å)	13.69310(10)	11.3452(2)	8.5423(2)
b (Å)	21.8126(3)	13.1943(2)	14.1815(4)
c (Å)	14.8774(2)	34.0928(6)	12.5693(3)
$\alpha = \gamma$ (deg)	90	90	90
β (deg)	113.9870(1)	90	92.4410(10)
V (Å^3)	4059.85(8)	5103.42(15)	1521.30(7)
Z	8	8	4
cryst size (mm)	0.28 × 0.28 × 0.28	0.25 × 0.25 × 0.1	0.25 × 0.25 × 0.25
D_{calc} (g cm^{-3})	1.348	1.473	1.554
temp (K)	198(2)	198(2)	198(2)
2θ scan range (deg)	7.04−55.0	7.14−57.36	7.10−54.94
index ranges	$-17 \le h \le 16$	$-15 \le h \le 7$	$-10 \le h \le 10$
	$-28 \le k \le 21$	$-17 \le k \le 17$	$-17 \le k \le 18$
	$-17 \le l \le 19$	$-46 \le l \le 46$	$-16 \le l \le 14$
no. of rflns collcd	37 781	37 804	17 111
no. of indpt reflns	9143	6407	3440
	$R_{int} = 0.0994$	$R_{int} = 0.0871$	$R_{int} = 0.0411$
final R1	0.0404	0.0529	0.0450
final wR2	0.0712	0.0979	0.1102
GOF	1.021	1.035	1.116
min./max. resid density (e Å^{-3})	−0.712, 0.989	−0.628, 0.612	−0.858, 1.461

1.410(6); C2−C3 1.408(6) Å], and the C1−C2−C3 angle [115.8°] is close to 120°, as typically observed in η^3-allyl ruthenium structures. The same conformation was found in solution, in agreement with previous reports of related compounds and consistent with the d^4 configuration of the ruthenium atom.[2a,5h,i,23a,24] The localized C=C bond, as expected, is the shortest [C4−C5 1.339(6) Å].

The centroid Cp*−Ru distance in **6** is 1.878 Å, which can be considered as an intermediate value to those of similar dienyloxy derivatives, such as Cp*Ru(η^3-*endo*-*syn*-CH$_2$CHCHCHO)Cl$_2$], (1.881 Å),[4] Cp*Ru{η^3-*endo*-*syn*-CH$_2$C(Me)CHC(Me)O}Cl$_2$ (1.889 Å),[4] and Cp*Ru{η^3-*endo*-*syn*-CH(Me)CHCHOEt}Cl$_2$ (1.864 Å).[4] The Ru−Cl bond distance for **6** [average: 2.4209(11) Å] is shorter than those corresponding to Ru(II) diene compounds **4** [2.4476(7) Å] and **8** [2.4484(12) Å] and longer than most η^3-allyl Ru(IV) compounds, such as [Cp*Ru(η^3-*endo*-C$_3$H$_5$)Cl$_2$] (2.408 Å),[24b] [CpRu(η^3-C$_4$H$_4$OMe)Cl$_2$] (2.403(1) Å),[24c] [Cp*Ru{η^3-*endo*-*anti*-CH$_2$C(Me)CHCH$_2$Cl}Cl$_2$] average (2.418(1) Å),[5i] and [Cp*Ru{η^3-*endo*-*anti*-CH$_2$C(Me)CHC(Me)O}(SnCl$_3$)(Cl)] (2.4002(9) Å),[2a] with the exception of [Cp*Ru{*endo*-*syn*-η^3-CH$_2$C(Me)CH-CH$_2$Cl}Cl$_2$] (2.4295(5) Å).[5i]

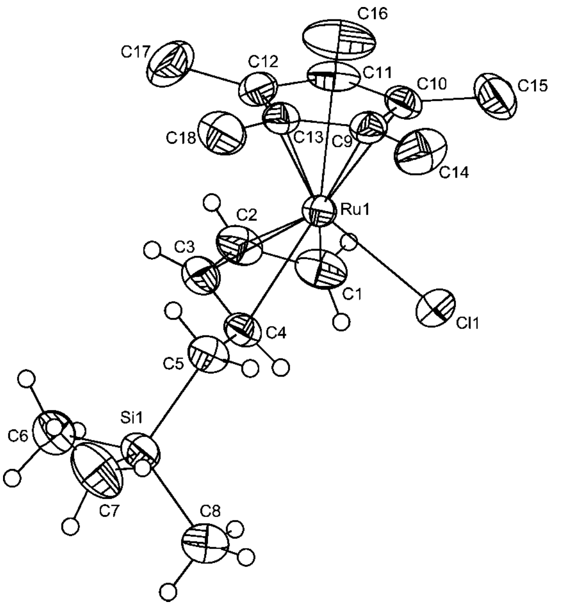

Figure 1. Crystal structure of [Cp*Ru(η^4-CH$_2$CHCHCHCH$_2$-SiMe$_3$)Cl] (**4**). Cp* hydrogen atoms have been omitted for clarity.

Experimental Section

General Remarks. All experiments were carried out under nitrogen or argon atmospheres using glovebox and standard Schlenk techniques. Solvents were distilled from Na/benzophenone (THF) or Na (diethyl ether) under nitrogen before use. Deuterated solvents were degassed. NMR spectra were recorded with Jeol GSX-270, Eclipse-400, and Bruker 300 spectrometers in CDCl$_3$, C$_6$D$_6$, and CD$_3$COCD$_3$. All chemical shifts are reported in ppm with reference to TMS. IR spectra were recorded in KBr pellets on a Perkin-Elmer Spectrum GX spectrophotometer. Elemental analyses were performed at the Chemistry Department of Cinvestav with a Thermo-Finnigan Flash 112 and at Desert Analytics, Tucson, AZ. Mass spectra were obtained with a Hewlett-Packard HP-5990A instrument. Ionization was by FAB with xenon atoms at 6 keV energy (Washington University, St. Louis, MO). Reagents RuCl$_3 \cdot$3H$_2$O, aluminum oxide (activated neutral Brockman I), and silica gel (Merck, 0.04−0.063) were used as received. The (Cp*RuCl)$_4$ (**1**),[1a,b]

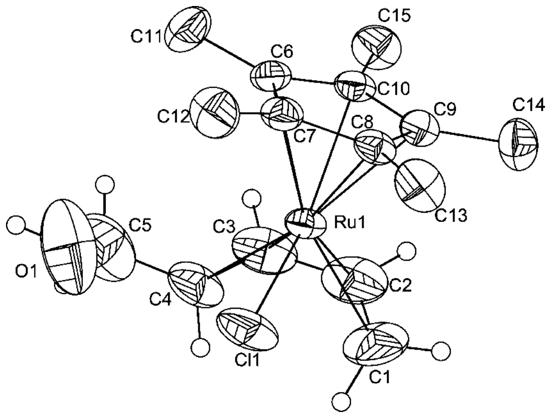

Figure 2. Crystal structure of [Cp*Ru(η^4-CH$_2$CHCHCHCH$_2$OH)Cl] (**8**). Cp* and OH hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengths and Bond Angles of Compounds 4 and 8

bond lengths (Å)			bond angles (deg)		
	4	**8**		**4**	**8**
C1−C2	1.390(5)	1.429(10)	C1−C2−C3	121.1(3)	119.6(6)
C2−C3	1.431(5)	1.403(10)	C2−C3−C4	121.4(3)	120.6(6)
C3−C4	1.387(4)	1.379(8)	C3−C4−C5	122.6(3)	124.0(6)
C4−C5	1.484(4)	1.451(10)	C1−C2−Ru1	73.29(19)	72.5(3)
C1−Ru1	2.204(3)	2.207(6)	C1−Ru1−Cl1	84.70(11)	85.02(2)
C2−Ru1	2.156(3)	2.167(5)	C4−Ru1−Cl1	81.05(8)	82.82(16)
C3−Ru1	2.190(3)	2.159(5)	C1−Ru1−C4	79.55(13)	78.7(3)
C4−Ru1	2.282(3)	2.225(5)	C4−C5−Si1	112.8 (2)	
Cl1−Ru1	2.4476(7)	2.4484(12)	C4−C5−O1		111.0(6)
C9−Ru1	2.233(4)	2.213(4)			
C5−Si1	1.882(3)				
C5−O1		1.460(10)			

$(Cp^*RuCl_2)_2$ (**2**),[5c] and $CH_2CHCHCHCH_2SiMe_3$ (**3**)[12a] reagents were synthesized using literature procedures.

Synthesis of [Cp*Ru(η^4-$CH_2CHCHCHCH_2SiMe_3$)Cl] (4). A THF solution (2 mL) of **3** (0.17 mL 0.98 mmol) was added to a red-brown solution of THF (15 mL) containing 266 mg (0.98 mmol) of compound **1** at −110 °C; the brown solution turned yellow-brown. After the mixture was stirred for 1 h at room temperature, the solvent was evaporated under reduced pressure and the residue was extracted with hexane (30 mL). The hexane solution was chromatographed on a column (2 × 20) packed with neutral Al_2O_3, and a yellow band was collected with a mixture of hexane/diethyl ether (7:3). The solution was concentrated (∼3 mL), and compound **4** was obtained as an orange-yellow powder in 50% yield (201 mg, 0.48 mmol), after the lower surface of the Schlenk vessel was sumerged into liquid nitrogen for a few minutes and the mixture of the oily compound **4** and hexane was frozen. Then, it was rubbed with a magnetic stirring bar until the residue remained as a solid, which has a melting point of 70−72 °C. Anal. Calcd for $C_{18}H_{31}Ru_1Cl_1Si_1$: C, 52.47; H, 7.58. Found: C 52.12, H 7.72. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 51.4 (C1), 87.3 (C2), 93.7 (C3), 77.4 (C4), 21.8 (C5), 93.7 (C, Cp*), 9.6 (Me, Cp*), −1.7 ($SiMe_3$). ^{29}Si ($CDCl_3$): δ 0.47. ^{29}Si (C_6D_6): δ −0.24. IR (KBr) cm^{-1}: 2955 (m), 2903 (m), 1454 (m), 1380 (m), 1246 (s), 856 (s, br). MS (20 eV): *m/z* 412 (7) [M^+], 73 (100), 376 (7), 303 (5), 276 (10), 236 (26), 140 (80).

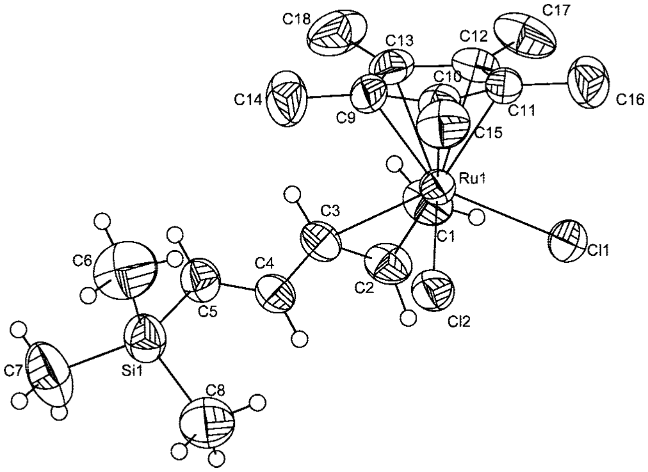

Figure 3. Crystal structure of [Cp*Ru(η^3-*endo-syn*-$CH_2CHCHCHCHSiMe_3$)Cl_2] (**6**). Cp* hydrogen atoms have been omitted for clarity.

Table 4. Selected Bond Lengths and Bond Angles of Compound 6

bond lengths (Å)		bond angles (deg)	
C1−C2	1.410(6)	C1−C2−C3	115.8(4)
C2−C3	1.408(6)	C2−C3−C4	124.8(4)
C3−C4	1.442(6)	C2−C1−Ru1	69.3(2)
C1−Ru1	2.186(4)	C4−C3−Ru1	121.2(3)
C2−Ru1	2.141(4)	Cl1−Ru1−Cl2	83.29(5)
C3−Ru1	2.301(4)	C1−Ru1−Cl1	80.99(14)
Cl1−Ru1	2.4216(12)	C3−Ru1−Cl1	124.70(12)
Cl2−Ru1	2.4202(11)	C2−Ru1−C3	36.74(16)
C4−C5	1.339(6)	C1−Ru1−C3	64.24(17)
C5−Si	1.850(5)	C1−Ru1−C10	148.55(16)
C9−Ru1	2.219(4)	C3−C4−C5	124.7(4)
C10−Ru1	2.301(4)	C4−C5−Si1	125.6(4)
C11−Ru1	2.272(4)	C1−Ru1−Cl2	126.54(12)
C12−Ru1	2.183(4)	C2−Ru1−Cl1	89.94(14)
C13−Ru1	2.190(4)	C1−C2−Ru1	72.7(2)
		C3−C2−Ru1	77.8(2)
		C2−Ru1−Cl2	91.61(14)

Syntheses of [Cp*Ru(η^4-$CH_2CHCHCHCH_2SiMe_3$)Cl] (4), [Cp*Ru(η^3-$CH_2CHCHCHCH_2$)Cl_2] (5), and [Cp*Ru(η^3-$CH_2CHCHCHCHSiMe_3$)Cl_2] (6). Compound **3** (0.22 mL, 1.30 mmol) was slowly added to a stirred solution of 200 mg (0.65 mmol) of **2** in 25 mL of THF at −78 °C. The mixture was warmed slowly to room temperature, and the dark brown solution turned red-brown. After 17 h of stirring, the mixture was filtered and the solvent was removed under vacuum. The residue was extracted with hexane (2 × 10 mL). The solution was concentrated as a mixture of compounds **4** and **6**. Further elution through a silica gel column (14 × 2) with diethyl ether allowed the separation of both compounds. Two bands were collected and evaporated to dryness; the first yellow band corresponded to compound **4** and the second orange band to **6**. Single crystals of the orange compound **6** were grown by cooling a saturated $CHCl_3$/hexane to −5 °C, in 20% yield (58.8 mg, 0.14 mmol). Mp: 169−172 °C.

The remaining orange solid, which was insoluble in hexane, was a mixture of compounds **5** and **6**. These compounds were separated on a silica gel column, **5** being eluted first with diethyl ether, while **6** remained on the column.

Syntheses of [Cp*Ru(η^4-$CH_2CHCHCHCH_2SiMe_3$)Cl] (4) and [Cp*Ru(η^3-$CH_2CHCHCHCH_2$)Cl_2] (5). Compound **3** (0.18 mL, 1.0 mmol) dissolved in 2 mL of EtOH was added to a solution of **2** (300 mg, 0.98 mmol) in 25 mL of EtOH at −110 °C. After being warmed to room temperature, the mixture was stirred for 2.5 h. Solid materials were removed by filtration, and the solvent was removed under reduced pressure. The remaining orange-brown residue was extracted with hexane (3 × 5 mL); the solution was concentrated and compound **4** was obtained by cooling the solution to −5 °C. Orange crystals, with a melting point 70−72 °C, were isolated in 30% yield (120 mg, 0.29 mmol). The residual material, which was insoluble in hexane, was crystallized from CH_2Cl_2 and hexane at −5 °C; compound **5** was obtained as wine-red needles, in 47% yield (172 mg, 0.46 mmol). **5** does not melt or decompose up to at least 192 °C. Anal. Calcd for $C_{15}H_{22}Cl_2Ru\cdot 1/4C_6H_{12}$: C, 50.0; H, 6.49. Found: C, 49.84; H, 6.49. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 64.8 (C1), 96.1 (C2), 86.8 (C3), 138.8 (C4), 120.5 (C5), 104.0 (C, Cp*), 9.8 (Me, Cp*). IR (KBr) cm^{-1}: 3077 (vs), 3017 (m), 2992 (m), 2963 (m), 2908 (m), 1899 (m), 1625 (m), 1453 (s), 1488 (s), 1076 (m), 1020 (s).

Synthesis of [Cp*Ru(η^3-$CH_2CHCHCHCHSiMe_3$)Cl_2] (6). An orange solution of **4** (62 mg, 0.15 mmol) in 20 mL of $CHCl_3$, maintained under reflux for 28 h, turned dark brown-red, after which it was filtered through a pad of Celite, and the solution was evaporated to dryness under vacuum. Diethyl ether was added to the oily brown residue, the solution was concentrated, and it was purified on a silica gel column through elution with diethyl ether. An orange fraction was collected, and the solvent was removed under reduced pressure; this gave compound **6** as orange needles, in 25% yield (16.8 mg, 0.037 mmol). Anal. Calcd for $C_{18}H_{30}Cl_2Si_1Ru \cdot CHCl_3$: C, 40.32; H, 5.52. Found: C, 40.50; H, 5.52. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 64.5 (C1), 95.5 (C2), 88.5 (C3), 145.5 (C4), 140.8 (C5), 105.7 (C, Cp*), 9.4 (Me, Cp*) 1.2 ($SiMe_3$). ^{29}Si NMR ($CDCl_3$): δ −5.6. ^{29}Si NMR (C_6D_6): δ −6.0. IR (KBr, cm^{-1}): 2955 (m), 2908 (w, br), 1481 (m, br), 1380 (m), 1246 (m), 865 (s), 840 (s). MS (20 eV): *m/z* 446 (5) [M^+]; 73 (100), 411 (3), 375 (13), 359 (10), 315 (3), 301 (14), 272 (16), 263 (13).

Transformation of Compound Cp*Ru(η^3-*endo-syn*-$CH_2CHCHCHCH_2$)Cl_2 (5) into Compounds Cp*Ru(η^3-$CH_2CHCHCH_2CH_3$)Cl_2 (7), Cp*Ru(η^4-$CH_2CHCHCHCH_2OH$)Cl (8), Cp*Ru(η^4-$CH_2CHCHCHCHO$)Cl (9), and 2,4-Pentadienal. (a) Compound **5** was crystallized from 3 mL of CH_2Cl_2 and 20 mL of hexane. After 20 days at −5 °C, compound **5** precipitated as a wine-red-colored powder. After several precipitations of **5**, ∼5 mg of **7** was obtained, from the same mother liquor, as a red-brown powder, which decomposes between 135 and 150 °C. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 65.3 (C1), 97.3 (C2), 92.0 (C3), 25.3 (C4), 15.5 (C5), 103.7 (C, Cp*), 9.9 (Me, Cp*). HR-FAB-MS (matrix: 3-NBA/Li): *m/z* 383(100) [$M^+ + Li$].

(b) A solution of **5** (50 mg 0.13 mmol) in 5 mL of acetone and CH_2Cl_2 (1:1) was applied to a preparative silica gel plate using $CHCl_3$/acetone (8:2) as eluent. An orange band was eluted and the solvent removed under vacuum to give an orange powder. After recrystallization from CH_2Cl_2/hexane, at −5 °C, 14 mg (0.05 mmol) of orange-red crystals of compound **8** was isolated in 30% yield. Mp: 179−181 °C dec. Anal. Calcd for $C_{15}H_{23}ClORu$: C, 50.62; H, 6.51. Found: C, 50.16; H, 6.74. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 53.8 (C1), 88.5 (C2), 91.5 (C3), 74.8 (C4), 63.9 (C5), 96.3 (C, Cp*), 9.9 (Me, Cp*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 53.3 (C1), 87.8 (C2), 91.3 (C3), 75.4 (C4), 63.8 (C5), 95.7 (C, Cp*), 9.6 (Me, Cp*). IR ($CHCl_3$) cm^{-1}: 3465 (w), 2960 (w), 2918 (w), 2862 (w), 1657 (m), 1485 (m). MS: *m/z* 356(3) [M^+], 320(2), 303(6), 290(6), 271(18), 236(32), 84(56), 55(100).

Identification of Compound 9 and 2,4-Pentadienal. Compound **8** (5.00 mg, 0.014 mmol) was dissolved in C_6D_6 (1 mL) inside an unsealed NMR tube. Gradually, the orange solution turned orange-red. After 15 days at room temperature, there was spectroscopic evidence of the aldehyde **9**, which after 10 days was completely consumed, and the ^1H and ^{13}C NMR spectroscopy showed the presence of $CH_2CHCHCHCHO$. Compound **9**: $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 57.6 (C1), 92.3 (C2), 89.7 (C3), 65.5(C4), 193.9 (C5), 97.6 (C, Cp*), 9.3 (Me, Cp*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 57.1 (C1), 92.0 (C2), 89.9 (C3), 65.9 (C4), 194.0 (C5), 96.5 (C, Cp*), 9.2 (Me, Cp*). 2,4-Pentadienal: see ref 22.

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Supporting Information Available: X-ray crystallographic data for compounds **4**, **6**, and **8** and NMR spectra of compound **9** and 2,4-pentadienal. This information is available free of charge via the Internet at http://pubs.acs.org

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