Comparative Study of the Reactivity of (Cp*RuCl)4 and (Cp*RuCl2)2 with Trimethylsilyl-Substituted Oxodienyl Ligands⊥

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Comparative Study of the Reactivity of $(Cp^*RuCl)_4$ and $(Cp^*RuCl_2)_2$ with Trimethylsilyl-Substituted Oxodienyl Ligands[⊥]

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A comparative study of the chemical reactivity of the well-known precursors $[Cp^*RuCl]_4$ (**1**) and $[Cp^*RuCl_2]_2$ (**2**) is established relative to the incorporation of silyl-substituted heterodienyl compounds. This study gives clear evidence of the influence of the solvents and the oxidation state of **1** versus **2** on these reactions. In THF, tetramer **1** reacts selectively with $CH_2CHCHCHOSiMe_3$ (**3**) to afford $[Cp^*Ru(\eta^4\text{-}CH_2CHCHCHOSiMe_3)Cl]$ (**4**), while the reaction of dimer **2** leads to nonselective reactions with the formation of **4** and $[Cp^*Ru(\eta^3\text{-}CH_2CHCHCHO)Cl_2]$ (**5**). Compound **5** is thermodynamically more stable than **4**. The reactivity of **1** and the mixture of isomers $CH_2C(Me)CHC(OSiMe_3)Me$ (**6a**) and $MeC(Me)CHC(OSiMe_3)CH_2$ (**6b**) affords oxo- and pentadienyl compounds $[Cp^*Ru\{\eta^5\text{-}CH_2C(Me)CHC(OSiMe_3)CH_2\}]$ (**7**), $[Cp^*Ru(\eta^5\text{-}CH_2C(Me)CHC(Me)O]$ (**8**), and $[Cp^*Ru\{\eta^3\text{-}exo\text{-}syn\text{-}CH_2C(Me)CHC(Me)O\}Cl_2]$ (**9**). The treatment of **2** with **3** in methanolic or ethanolic solutions at room temperature provided a preparative route to the corresponding (allyl)ruthenium(IV) species: **5**, $[Cp^*Ru\{\eta^3\text{-}endo\text{-}CH(Me)CHCHOR\}Cl_2]$ [R = Me (**10**); R = Et (**12**)]; $[Cp^*Ru\{\eta^3\text{-}endo\text{-}CH_2CHCHCH(OR)_2\}Cl_2]$ [R = Me (**11**); R = Et (**13**)]. The ratio of the species formed could change significatively depending on the ratios of reactants or reaction conditions. The acetal derivatives **10**−**13** are generated as the result of nucleophilic attack of the alcohols on compound **5**. When zinc is used as a reducing agent in ethanol, compound **2** reacts with **3** or the mixture of **6a** and **6b** to give trimetallic compounds $Cp^*Ru[\eta^5\text{-}CH_2C(R)CHC(R)O]_2(\mu_2\text{-}ZnCl_2)$ (R = H, **14**; R = Me, **15**), which have a $ZnCl_2$ bridging two $Cp^*Ru[\eta^5\text{-}CH_2C(R)CHC(R)O]$ molecules through the oxygen atoms of the corresponding oxopentadienyl ligands, along with $[Cp^*Ru\{\eta^4\text{-}CH_2C(R)CHC(R)X\}Cl]$ [R = H, X = OEt, **17**; R = Me, X = OH, **18**] as minor products. **15** reacts in the presence of $CDCl_3$ to give the oxidative addition products *exo-syn*-**9** and $[Cp^*Ru\{\eta^3\text{-}endo\text{-}anti\text{-}CH_2C(Me)CHC(Me)O\}Cl_2]$ (**19**). All compounds have been fully characterized by ^1H and ^{13}C NMR spectroscopy, and the crystal structures of **5**, **9**, **12**, and **15** are also described.

Introduction

The chemistry of ruthenium complexes of the pentamethylcyclopentadienyl (Cp*) ligand has been basically developed from $(Cp^*RuX_2)_2$ (X = Cl, Br, I),[1−5] which reacts with a great number of ligands to generate a wide range of half-sandwich[2,3c,6−12] and half-open sandwich compounds.[13−17] In the presence of reducting agents such as zinc[18] or Et_3BHLi,[8] $(Cp^*RuCl_2)_2$ affords the tetramer $(Cp^*RuCl)_4$,[8,19] and in the presence of K_2CO_3 in methanol or ethanol this gives dimeric derivatives $(Cp^*RuOR)_2$ (R = Me, Et),[3,11] each of these compounds being representative of the broad area of Cp*Ru chemistry. However, the chloride derivatives $(Cp^*RuCl_2)_2$ and $(Cp^*RuCl)_4$ are particularly useful. The degree of oligomerization of the complex

[⊥] Dedicated to the memory of Professor Fred Basolo.

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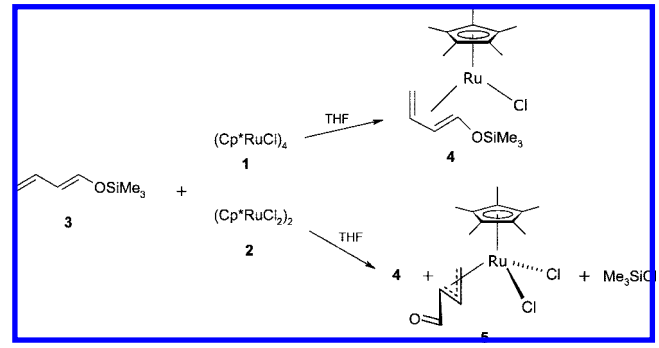
$(Cp^*RuCl_2)_n$[4] depends on the synthetic procedure.[1−3,5] When $(Cp^*RuCl_2)_n$ is purified by silica gel chromatography (treated with Me_3SiCl), the corresponding dimer can be separated from other oligomeric fractions of higher molecular weights, and the crystallization of the dimer in CH_2Cl_2/Et_2O allows the crystallographic study of "deformation isomers" with different angles and bond distances between the ruthenium and chloride atoms.[4] Usually, for synthetic purposes the oligomeric mixture is used directly. However, in most of the cases it is represented as a dimer, as it will be considered throughout this work.[3a]

The half-open sandwich compounds Cp*Ru(2,4-dimethyl-η^5-oxopentadienyl) (**8**)[13,15] and Cp*Ru(η^5-oxopentadienyl) (**16**)[20] have already been prepared by various synthetic methods,[13−15] from $(Cp^*RuCl)_4$ and lithium 2,4-dimethyloxopentadienide,[15] mesityl oxide,[13] or trimethylsiloxybutadiene,[20] respectively. The latter $CH_2{=}CHCH{=}CHOSiMe_3$ ligand also has been shown to lead to Cp*Ru(η^4-$CH_2{=}CHCH{=}CHOSiMe_3$)Cl, which disproportionates to Cp*Ru(η^5-$CH_2CHCHCHO$) and [Cp*Ru(η^3-$CH_2CHCHCHO$)Cl_2]. After purification by chromatography, the corresponding Cp*Ru(η^5-$CH_2CHCHCHO$) (**16**) can be obtained in a moderate yield (69%);[20] however, this compound cannot be isolated if crotonaldehyde is used as a ligand in the presence of **1**.[11,20,21]

It is well known that trimethylsiloxy substituents have interesting properties, such as the versatility to transform into different organic groups and a strong π donor ability.[22] There appear to be few examples of trimethylsiloxybutadiene as ligands with transition metal complexes, and in fact, it has been observed that most of the reactions with such molecules have led to loss of the $SiMe_3$ fragment through O−Si bond cleavage. For example, studies by Green and co-workers showed that the reactions of $CH_2CHCHCHOSiMe_3$ with $[Cp^*Mo(NCMe)_2(CO)_2]BF_4$ and $[CpRu(CO)(MeCN)_2]^+$ afforded mixtures of three isomers for Cp*Mo(CO)$_2$(η^3-$CH_2CHCHCHO$)[23] but two isomers for CpRu(CO)(η^3-$CH_2CHCHCHO$).[24] Similarly, the dimer [Pd(η^3-$CH_2CHCHCHO$)Cl]$_2$ was isolated by Murai et al.[25] as a 6.7/1.0 *syn/anti* mixture of isomers from the reaction of $[PdCl_2(MeCN)_2]$ with the trimethylsiloxybutadiene ligand. Finally, the studies carried out by Ernst and co-workers on the reaction of 2-siloxy-4-methyl-1,3-pentadiene with $[Cp^*RuCl]_4$ revealed that an isolable Cp*RuCl(η^4-diene) complex is initially formed, which subsequently loses HCl, leading to the expected Cp*Ru(2-siloxy-4-methyl-η^5-pentadienyl) compound.[17] Subsequent work with siloxy-substituted 1,3- or 1,4-dienes showed the incorporation of the organic fragment could occur as either a diene or dienyl ligand.[26] In order to gain further knowledge about the oxopentadienyl ligands as well as an improved understanding of the role of the $SiMe_3$ group and the influence on the oxidation state of these ruthenium compounds, we decided to pursue a comparative study of the reactions of $(Cp^*RuCl_2)_2$ or $(Cp^*RuCl)_4$ with trimethylsiloxybutadiene ligands. It is interesting to observe the unexpected chemistry that the Cp*Ru fragment reveals using these two common and well-known precursors. The influence of the solvent in these reactions is also considered.

Scheme 1



Some compounds of this work has been previously described in a review of half-open metallocenes with heterodienyl ligands.[27]

Results

Reactivity of $(Cp^*RuCl)_4$ (1) and $(Cp^*RuCl_2)_2$ (2) toward Trimethylsiloxybutadiene (3). (a) Reactions in THF. The complex $(Cp^*RuCl)_4$ (**1**) reacts readily with $CH_2{=}CHCH{=}CHOSiMe_3$ (**3**) under very mild conditions to form [Cp*Ru(η^4-$CH_2CHCHCHOSiMe_3$)Cl] (**4**),[20] which can be isolated as bright orange crystalline solid in 88% yield, Scheme 1. In contrast to this result, the reaction of $(Cp^*RuCl_2)_2$ (**2**) with **3**, at room temperature, leads to a nonselective reaction with the formation of two compounds, **4** and [Cp*Ru(η^3-$CH_2CHCHCHO$)Cl_2] (**5**),[20] in a 0.9:1.0 ratio (Scheme 1).

Compounds **4** and **5** could be separated due to solubility differences. Thus, while **4** was soluble in hexane (40% yield), **5** could be purified by preparative silica gel chromatography with acetone/ethyl acetate (8:2) as eluents, leading to its isolation from $CHCl_3$/hexane in a 56% yield.

The selectivity of the conversion of the tetramer $(Cp^*RuCl)_4$ to the low oxidation state species **4** contrasts with the behavior of the dimer $(Cp^*RuCl_2)_2$, which leads to the formation of Ru(II) and Ru(IV) compounds **4** and **5**, respectively. Compound **5** is thermodynamically more stable than **4**, and this is attributed to the presence of the trimethylsiloxy group in the dienyl ligand in **4**, within which $SiMe_3$ can easily react with nucleophiles, including the intramolecular chloride ligand to give Me_3SiCl. It is important to mention that compound **4** can disproportionate[20] to Cp*Ru(η^5-$CH_2CHCHCHO$) (**16**) and **5** (*vide infra*), where the former can easily be transformed to **5** by oxidative addition in the reaction medium.

The ^1H, ^{13}C, and ^{29}Si NMR data of compounds **4** and **5** are described in Tables 1 and 2, respectively, and the molecular structure of **5** in the solid state confirms the presence of the η^3-*endo-syn* conformation.

The reaction of **1** and the mixture of 1,3-dimethylbutadienyloxytrimethylsilane (**6a**) and 4-methyl-2-trimethylsililoxy-1,3-pentadiene (**6b**) isomers afforded the pentadienyl compound [Cp*Ru{η^5-$CH_2C(OSiMe_3)CHC(Me)CH_2$}] (**7**) and the oxopentadienyl compounds [Cp*Ru(η^5-$CH_2C(Me)CHC(Me)O$] (**8**)

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Table 1. ^{1}H NMR Data[a] for Compounds 4, 5, 7−18, 22, and 23

compound	H_{1a}	H_{1s}	H_2 or Me2	H_3	H_4 or Me_4	H_5	Cp*
4[b,c]	1.35 (dd) $J_{H1a,H1s} = 1.7$ $J_{H1a,H2} = 10.6$	2.96 (dd) $J_{H1a,H1s} = 1.7$ $J_{H1s,H2} = 7.7$	4.17 (m)	4.60 (m)	4.61 (d)		1.61 (s)
4[c,d]	1.75 (dd) $J_{H1a,H1s} = 1.8$ $J_{H1a,H2} = 10.5$	2.85 (dd) $J_{H1a,H1s} = 1.8$ $J_{H1s,H2} = 7.7$	3.75 (ddd) $J_{H1a,H2} = 10.5$ $J_{H1s,H2} = 7.7$ $J_{H2,H3} = 5.8$	4.50 (dd) $J_{H2,H3} = 5.7$ $J_{H3,H4}$= 7.5	4.98 (d) $J_{H3,H4} = 7.5$		1.38 (s)
5[b]	2.40 (d) $J_{H1a,H2} = 9.7$	4.36 (d) $J_{H1s,H2} = 6.4$	6.15 (ddd) $J_{H1a,H2} = 9.7$ $J_{H1s,H2} = 6.2$ $J_{H2,H3} = 9.7$	2.55 (dd) $J_{H2,H3} = 9.5$ $J_{H3,H4} = 7.1$	10.14 (d) $J_{H3,H4} = 7.1$		1.64 (s)
5[d]	1.58 (d) $J_{H1a,H2} = 9.7$	4.08 (d) $J_{H1s,H2} = 6.2$	5.83 (m)	1.99 (dd) $J_{H2,H3} = 9.5$ $J_{H3,H4}$= 7.1	10.28 (d) $J_{H3,H4} = 7.3$		1.00 (s)
7[c]	−0.37 (d) $J_{H1a,H1s} = 2.2$	1.91 (d) $J_{H1a,H1s} = 2.2$	4.89 (s)	1.82 (s)		− 0.02 (d) $J_{H5a,H5s} = 3.7$ 2.22 (d) $J_{H5a,H5s} = 3.7$	1.77 (s)
7[c,d]	0.04 (d) $J_{H1a,H1s} = 2.1$	2.17 (d) $J_{H1a,H1s} = 2.4$	5.09 (s)	1.80 (s)		0.29 (d) $J_{H5a,H5s} = 3.6$ 2.48 (d) $J_{H5a,H5s} = 3.7$	1.77 (s)
8[e]	1.58 (s)	3.10 (s)	1.99 (s)	4.80 (s)	1.54 (s)		1.68 (s)
8[d,e]	2.28 (s)	3.25 (s)	1.96 (s)	4.68 (s)	1.48 (s)		1.59 (s)
9[e]	2.17(s)	3.80 (s)	2.60 (s)	2.80 (s)	2.40 (s)		1.61 (s)
10	2.57 (m)	1.65 (d) $J_{H1a,Me1s} = 6.2$	5.05 (t) $J_{H1a,H2} = 9.0$ $J_{H2,H3} = 9.0$	5.30 (d) $J_{H2,H3} = 9.0$	3.76 (s)		1.60 (s)
11	2.27 (d) $J_{H1a,H2} = 9.4$	4.19 (d) $J_{H1s,H2} = 6.1$	5.32 (m)	2.80 (dd) $J_{H2,H3} = 10.0$ $J_{H3,H4} = 6.0$	5.14 (d) $J_{H3,H4} = 6.1$	3.44 (s) 3.50 (s)	1.64 (s)
12	2.56 (dq) $J_{H1a,Me1s} = 6.2$ $J_{H1a,H2} = 9.6$	1.62 (d) $J_{H1a,Me1s} = 6.2$	5.00 (t) $J_{H1a,H2} = 9.3$ $J_{H2,H3} = 9.3$	5.37 (d) $J_{H2,H3} = 8.8$	4.05 (m) 3.91 (m)	1.33 (t) $J_{H4',H5} = 7.0$ $J_{H4'',H5} = 7.0$	1.58 (s)
12[d]	1.92 (m)	1.64 (d) $J_{H1a,Me1s} = 6.2$	5.03 (t) $J_{H1a,H2} = 9.1$ $J_{H2,H3} = 8.6$	4.90 (d) $J_{H2,H3} = 8.8$	4.08 (m) 3.52 (m)	1.12[f]	1.11 (s)
13[g]	2.27 (d) $J_{H1a,H2} = 9.5$	4.18 (dd) $J_{H1a,H1s} = 0.6$ $J_{H1s,H2} = 6.1$	5.23 (m)	2.85 (dd) $J_{H2,H3} = 10.3$ $J_{H3,H4} = 6.6$	5.25 (d) $J_{H3,H4} = 6.6$	3.65 (m) 3.58 (m) 3.77 (m)	1.63 (s)
13[d,g]	1.72 (d) $J_{H1a,H2} = 9.4$	4.20 (d) $J_{H1s,H2} = 6.6$	5.42 (ddd) $J_{H1a,H2} = 9.7$ $J_{H1s,H2} = 6.0$ $J_{H2,H3} = 9.8$	2.66 (dd) $J_{H2,H3} = 10.0$ $J_{H3,H4} = 6.4$	5.55 (d) $J_{H3,H4} = 6.3$	3.63 (m) 3.79 (m) 3.45 (m)	1.18 (s)
14[d]	2.14 (d) $J_{H1a,H2} = 11.0$	3.51 (d) $J_{H1s,H2} = 8.6$	3.31 (m)	4.01 (m)	4.34 (d) $J_{H3,H4} = 5.8$		1.61 (s)
15	1.88 (s)	3.58 (s)	1.66 (s)	4.82 (s)	2.18 (s)		1.64 (s)
15[d]	2.26 (s)	3.53 (s)	1.32 (s)	4.36 (s)	2.22 (s)		1.58 (s)
16[b]	1.72 (d) $J_{H1a,H2} = 10.9$	3.37 (d) $J_{H1s,H2} = 8.3$	4.46 (m)	4.88 (d) $J_{H2,H3} = 5.8$	6.88 (s, br)		1.84 (s)
16[d]	2.30 (d) $J_{H1a,H2} = 10.2$	3.37 (d) $J_{H1s,H2} = 8.5$	4.28 (m)	4.61 (d) $J_{H2,H3} = 6.6$	6.90 (s,br)		1.62 (s)
17[h]	1.37 (d,d) $J_{H1a,H2} = 10.2$	3.00 (d) $J_{H1s,H2} = 7.8$	4.23 (m)	4.52 (m)	4.61 (d) $J_{H3,H4} = 7.6$	3.72 (q) $J_{H5,H6} = 7.1$	1.65(s)
17[d,h]	1.75 (d) $J_{H1a,H1s} = 1.9$ $J_{H1a,H2} = 10.8$	2.87 (dd) $J_{H1a,H1s} = 1.2$ $J_{H1s,H2} = 6.7$	3.84 (m)	4.36 (m)	4.81 (d) $J_{H3,H4} = 7.5$	3.73 (m)	1.37(s)
18[i]	1.84 (s)	3.62 (s)	1.69 (s)	5.12 (s)	2.25 (s)		1.78 (s)
18[d,i]	1.57 (s)	3.56 (s)	1.41 (s)	5.67 (s)	1.86 (s)		1.66 (s)
19[e]	3.88 (s)	4.10 (s)	2.44 (s)	4.90 (s)	2.07 (s)		1.60 (s)
22[c]	1.40 (d) $J_{H1a,H1s} = 2.2$	3.19 (d) $J_{H1a,H1s} = 1.8$	4.82 (d) $J_{H1s,H2} = 1.5$	2.07 (s)			1.74 (s)
22[c,d]	2.01 (d) $J_{H1a,H1s} = 1.8$	3.34 (t) $J_{H1a,H1s} = 1.7$ $J_{H1s,H2} = 1.7$	4.89 (d) $J_{H1s,H2} = 1.5$	2.01 (s)			1.65 (s)
23[c,j]	−0.35 (s)	3.37 (s)	5.21 (s)	1.46 (s)			1.80 (s)
23[c,d,j]	0.03 (d) $J_{H1a,H1s} = 3.5$	2.44 (d) $J_{H1a,H1s} = 3.0$	5.32 (s)	1.85 (s)			1.83 (s)

[a] δ (ppm), $CDCl_3$. For numbering, see Schemes 3 and 4. [b] Reference 20. [c] ^{1}HNMR Si-Me_3 δ **4**: 0.21 (s)[a], 0.31 (s)[d]; **7**: 0.18 (s),[a] 0.24 (s);[d] **22**: 0.20 (s) [a], 0.17 (s)[d]; **23**: 0.10 (s)[a], 0.21 (s)[d]. [d] C_6D_6. [e] Reference 15. [f] Overlapped with Cp* signal. [g] Me_6 and $Me_{6'}$: [δ = 1.17 (t, J = 6.9), 1.26 (t, J = 6.9)[a]]; 1.13[d,f]. [h] Me: δ = 1.22 (t, J = 7.1)[a]; 1.10 (m)[d]. [i] $(CD_3)_2CO$; OH: δ = 3.44 (s,br); (not observed)[d]. [j] OH: δ = [9.23 (s,br)][a]; [5.30 (s,br)].[d]

Table 2. ^{13}C and ^{29}Si NMR Data[a] for Compounds 4, 5, 7−18, 22, and 23

compound	C1	C2	C3	C4	C5	C6	C(Cp*)	C(Me,Cp*)
4[b,c,d]	50.9	84.2	84.2	107.9			93.7	9.3
4[b,c,d,e]	50.8	83.7	84.4	108.6			94.0	9.5
5[b]	66.8	99.1	68.2	201.6			107.5	9.8
5[b,e]	66.3	98.6	68.2	201.0			106.4	9.2
7[c,d]	42.1	122.0	86.2	89.5	39.3	24.9	87.7	10.1
7[c,e]	43.0	122.0	86.4	89.5	39.8	15.2	86.8	10.1
8[e,f]	54.8	101.2	84.0	135.0	25.1	23.2	87.1	10.6
9[f]	66.7	110.1	70.1	205.7	34.7	18.4	106.5	9.5
10	16.6	68.2	84.5	126.8	60.7		100.3	9.8
11	66.0	95.6	81.9	104.7	54.5	55.7	105.4	10.4
12	16.5	68.2	84.2	127.0	69.2	14.5	100.2	9.6
13	66.0	103.0	95.0	82.5	63.0; 63.7	15.4; 15.6	105.2	9.7
13[e]	66.9	103.0	95.1	82.6	63.4; 62.9	16.0; 15.8	104.4	9.4
14[e]	58.3	90.8	88.6	118.0			92.4	10.9
15	60.0	104.4	87.1	127.6	25.7	22.8	89.5	10.9
16[b]	55.5	90.8	88.0	123.0			89.4	11.1
17	51.7	81.8	85.5	113.0	68.2	15.4	94.7	9.7
18[g]	59.1	96.6	86.9	104.7	24.4	21.6	89.1	9.8
19[f]	61.8	115.8	70.5	207.3	36.2	20.4	106.8	9.5
22[c,d,e]	48.5	128.9	79.5	132.2	23.6		87.4	10.6
23[c,d,e]	38.4	119.2	81.3	129.0	27.8		89.9	10.2

[a] δ (ppm), $CDCl_3$. For numbering, see Schemes 3 and 4. [b] Reference 20. [c] ^{13}C NMR Si-Me_3 δ **4**: 0.08[a]; 0.52[e]; **7**: 0.4[a], 0.2[e]; **22** 0.50[e]; **23**: 0.20[e]. [d] ^{29}Si NMR δ **4**: 23.3[a]; 22.9[e]; **7**: 17.4[a]; **22**: 18.8[e]; **23**: 18.1[e]. [e] C_6D_6. [f] Reference 15. [g] $(CD_3)_2CO$.

and [Cp*Ru{η^3-exo-syn-$CH_2C(Me)CHC(Me)O$}Cl_2] (**9**) in a 0.8:1.0:0.4 ratio, with 2, 20, and 17% yields, respectively (Scheme 2).

Compounds **8** and **9** have already been reported,[13,15] while compound **7** is related to the known [Cp*Ru{η^5-$CH_2C(Me)CHC(OSiMe_2t\text{-}Bu)CH_2$}].[17] The ^1H and ^{13}C NMR spectroscopy of compound **7** gave evidence of the η^5-pentadienyl coordination through the chemical shifts for the nonequivalent H_{1anti} and H_{5anti} protons, which appeared at δ 0.04 and 0.29, and the corresponding H_{1syn} and H_{5syn} signals at δ 2.17 and 2.48, as well as that of H_2 at δ 5.09. The methyl groups appear at δ 0.24, 1.77, and 1.80, with the former being assigned as the $OSiMe_3$ group. The Cp* quaternary carbon resonance (δ 86.8) further supported the formulation as a Ru(II) complex, and the presence of two methylene carbons confirmed the substitution of the $OSiMe_3$ in the pentadienyl ligand.

(b) Reactions in EtOH and MeOH. Reactions of **2** with **3**, in methanolic or ethanolic solutions at room temperature, provided a preparative route to (allyl)ruthenium(IV) species **5** [Cp*Ru{η^3-*endo*-CH(Me)CHCHOR}Cl_2] [R = Me (**10**), R = Et (**12**)] and [Cp*Ru{η^3-*endo*-$CH_2CHCHCH(OR)_2$}Cl_2] [R = Me (**11**); R = Et (**13**)] (Scheme 3).

After 7 h at room temperature, the ethanolic reaction mixture gave a 1.0:0.7:0.4 ratio of compounds **5**, **12**, and **13**, respectively. There was no evidence of the formation of **4** in this reaction, with only Ru(IV) species being observed.

Treatment with toluene, in which **5** is partially soluble, afforded soluble and insoluble fractions, which were purified by chromatography. The toluene-soluble fraction, with ethyl acetate and acetone as eluants, ultimately afforded orange-yellow needles of **13** and **12** as a yellow powder in 27 and 5% yields, respectively, while compound **5** was retained in the alumina. The toluene-insoluble fraction was chromatographed on a silica gel plate and afforded, with ethyl acetate/acetone (8:2), compound **5** in 15% yield. When the reaction was carried out with 3 equiv of the ligand, compounds **5** and **12** were obtained in a 1.0:0.6 ratio along with traces of **13**. Compound **5** was extracted with toluene, leading to a yield of 57%. The toluene-insoluble fraction afforded **12** and **13** in a 10:3 ratio, and after chromatography on silica gel, **12** was obtained in 17% yield, while **13** had decomposed.

When the reaction between **2** and **3** was carried out in refluxing ethanol, a mixture of **2**, **5**, **12**, and crotonaldehyde was observed through ^1H NMR spectroscopy. From this reaction only compound **12** was obtained, as an orange powder in 48% yield, after crystallization in $CHCl_3$/hexane.

From the spectroscopic results, it is possible to propose that **5** is formed first, which can undergo nucleophilic attack to afford **12**. The absence of **13** suggested that a different reaction mechanism proceeded for each acetal formed (*vide infra*). In order to confirm the aldehydic attack by the alcohol, compound **5** was refluxed 9 h in EtOH, which resulted clearly in the formation of **2** and **12**. From the above, it is proposed that **5** is the precursor of the corresponding acetals **12** and **13** by virtue of the sites available for electrophilic attack: the terminal allylic carbon atoms, the carbonyl group, the acetal carbon atom, and the metal center. This suggests the possibility of different reaction mechanisms in the case of the formations of **10** and **12** versus **11** and **13**, for which protonation can give different intermediates.

As already described, the acetal derivatives arise as a result of nucleophilic attack of the alcohols, to yield compound **5**. It is important to mention that acetals **10** and **12** are generated independently of diacetals **11** and **13**. There is ^1H NMR spectroscopy evidence that **11** is formed before **10**, and the amount of **11** can be increased at the expense of **5**, but not from **10**, which suggests that **10** and **11** follow different mechanistic reaction pathways (*vide infra*).

The reaction of $(Cp^*RuCl_2)_2$ (**2**) with a 30% excess of $CH_2CHCHCHOSiMe_3$ (**3**) in MeOH (from −110 °C until reaching room temperature after 30 min) shows, through ^1H NMR spectroscopy, the formation of a mixture of compounds: [Cp*Ru(η^3-$CH_2CHCHCHO$)Cl_2] (**5**), [Cp*Ru(η^3-*endo*-CH(Me)-$CHCHOMe)Cl_2$] (**10**), and [Cp*Ru(η^3-*endo*-$CH_2CHCHCH(OMe)_2$)Cl_2] (**11**) in a 0.3:1.0:2.0 ratio, respectively. The ratio changed to 0.7:1.0:0.9 after 4 h at room temperature. Compound **5** was extracted from toluene, purified via chromatography, and isolated in 37% yield; the acetal derivative **10** was insoluble in toluene; therefore it was extracted with diethyl ether to afford, after column chromatography, an 8% yield of yellow-orange crystals. Compound **11** was insoluble in toluene and diethyl ether, but it could be obtained as an orange-red powder in 13% yield by recrystallization from $CHCl_3$/hexane.

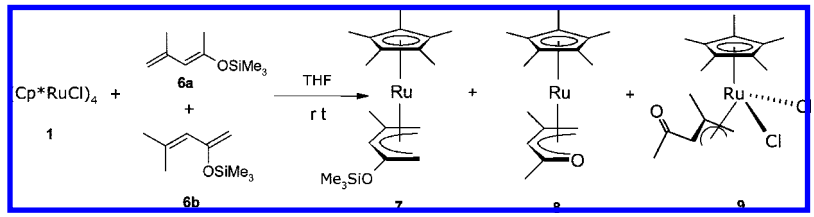
The acetal derivatives **10**−**13** showed a preferential *endo* conformation in their allylic fragments.

A similar reaction of the mixture of isomers **6a** and **6b** with **2** afforded the *exo-syn* compound **9** in a 25% yield, Scheme 3. This compound has also been isolated in a lower yield (4%), along with the *endo-anti* isomer.[15] In contrast, compound **9** in the solid state showed an *endo-syn* conformation (*vide infra*).

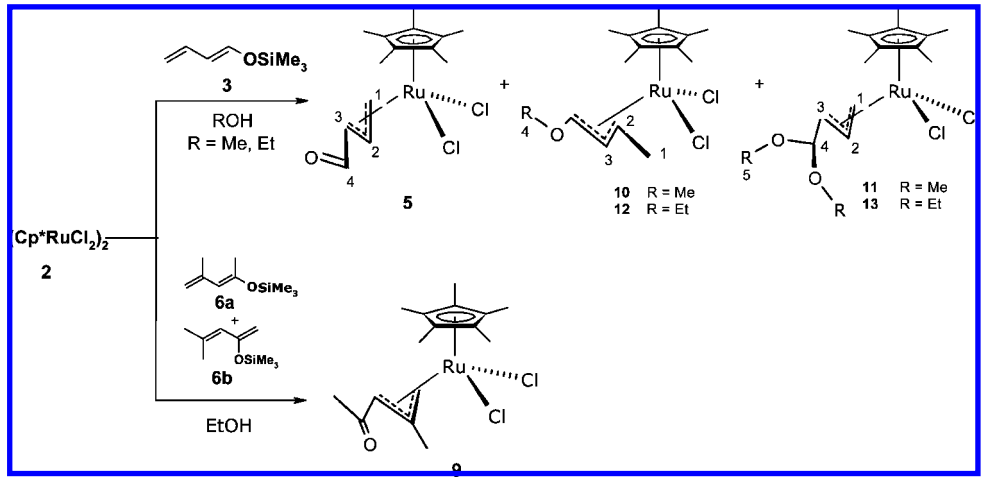
(c) Reactions in EtOH in the Presence of Zn as a Reducing Reagent. When reaction between **2** and **3** or the mixture of **6a**,**b** was carried out in ethanol using zinc as a reducing agent, trimetallic compounds Cp*Ru[η^5-$CH_2C(R)CHC(R)O]_2(\mu_2$-$ZnCl_2)$ (R = H, **14**; R = Me, **15**) were produced, along with [Cp*Ru{η^4-$CH_2C(R)CHC(R)X$}Cl] [R = H, X = OEt, **17**; R = Me, X = OH, **18**] as minor products, Scheme 4. The former two compounds were found to have a $ZnCl_2$ unit bridging two Cp*Ru[η^5-$CH_2C(R)CHC(R)O$] fragments [R = H, **16**; Me, **8**] through their oxygen atoms.

According to ^1H NMR spectroscopy, formation of compounds Cp*Ru[η^5-$CH_2CHCHCHO]_2(\mu_2$-$ZnCl_2)$ (**14**) and [Cp*Ru(η^4-

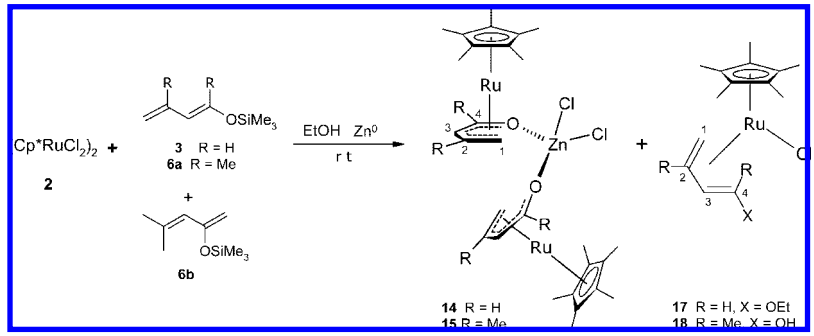
Scheme 2



Scheme 3



Scheme 4



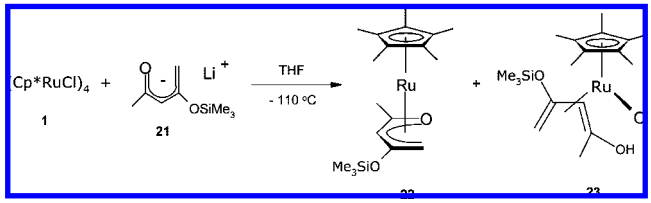
$CH_2CHCHCHOEt)Cl]$ (**17**) occurred in a 10:1 ratio. Compound **14** is partially soluble in diethyl ether, from which it afforded a yellow-orange precipitate in very low yield (~2%) after the solution was concentrated and cooled to −15 °C. The orange-brown powder, which remained insoluble in diethyl ether, was treated with acetone, and an oily residue was isolated by decantation after the addition of diethyl ether. After chromatography, the residue was observed to contain compounds **5** and Cp*Ru(η^5-$CH_2CHCHCHO$) (**16**)[20] in a 0.85:1.0 ratio. The diethyl ether-soluble products afforded a mixture of **16** and **17** in a 0.2:1.0 ratio. Compound **17** was characterized only through NMR spectroscopy, and it showed evidence of the ethoxy group [δ (^{1}H, ^{13}C, $CDCl_3$): 3.72(q), 1.22 (t); 68.2, 15.4] as a result of the favorable nucleophilic attack of ethanol on the delocalized carbonyl group in **14**. It is likely that the bridging $ZnCl_2$ molecule has diminished the electron density in the C═O moiety, in comparison to **16**.

A more robust analogous complex, **15**, was obtained when methyl groups were included as substituents in the oxopentadienyl ligand (Scheme 4). The reaction of **2** with the mixture of isomers **6a** and **6b** afforded, after 6 h at room temperature, a mixture of **15** and **18** in a 1.0:0.07 ratio, as detected through ^{1}H NMR spectroscopy. From this mixture, about 5 mg of pale yellow **18** was obtained from diethyl ether, whereas compound **15** was isolated in 31% yield from toluene and recrystallized from CH_2Cl_2/hexane as canary-yellow crystals. Compound **15** was unequivocally characterized, including its crystalline structure (*vide infra*); however, **18** was identified only by ^{1}H and ^{13}C NMR spectroscopy. When purification by chromatography on alumina was carried out for compound **15**, the formation of the well-known Cp*Ru[η^5-$CH_2C(Me)CHC(Me)O$] (**8**) was observed, which reflected the lability of the $ZnCl_2$ bridge. Also, compound **15** reacted in the presence of $CDCl_3$ to give the oxidative addition products *exo-syn*-**9** and [Cp*Ru{η^3-*endo-anti*-$CH_2C(Me)CHC(Me)O$}Cl_2] (**19**).[15]

Several attempts to remove chloride ions from **15** were unsuccessful because the formation of **8** was preferred even under very mild conditions. Addition of lithium oxopentadienide to **15** afforded **8** in 51% yield.

Reactivity of (Cp*RuCl)$_4$ (1) and (Cp*RuCl$_2$)$_2$ (2) toward Trimethylsiloxypentenone (20) and the Corresponding Lithium Anion (21). Considering the role of the methyl groups in the stabilization of compound **15**, the related reactions of 4-trimethylsiloxy-3-penten-2-one (**20**) with the corresponding [$CH_2C(OSiMe_3)CHC(Me)O$]Li (**21**) were explored in the presence of ruthenium compounds **1** and **2**. Surprisingly, the results showed that even though there were methyl groups that could stabilize the oxopentadienyl ligands, the presence of the silyloxy

Scheme 5



group seemed more important in determining the chemistry for these systems (*vide infra*).

In fact, $(Cp^*RuCl)_4$ (**1**) reacted in THF, under very mild conditions, readily with **21** to form $Cp^*Ru[\eta^5\text{-}CH_2C(OSiMe_3)CHC(Me)O]$ (**22**) and $[Cp^*Ru\{\eta^4\text{-}CH_2C(OSiMe_3)CHCMe(OH)\}Cl]$ (**23**) in a 1.0:0.1 ratio, Scheme 5. They were identified through ^1H and ^{13}C NMR spectroscopy as a mixture (≈8.0:0.3, respectively), because attempts at their separation through alternative techniques such as chromatography, sublimation, and crystallization were unsuccessful. Compound **23** decomposed on alumina, and while compound **22** could be isolated from diethyl ether in a very small amount, most of it remained on the chromatography column.

Contrastingly, compound **8** was quite stable, while **22** was much more fragile and decomposed at room temperature, even under nitrogen atmosphere.

A mixture of $(Cp^*RuCl_2)_2$ (**2**) and $[CH_2C(OSiMe_3)CHC(Me)O]$ (**20**) in EtOH, in the presence of zinc at room temperature, afforded $[Cp^*Ru(\eta^6\text{-}C_7H_8)]Cl$ (**24**)[18] as a yellow-orange powder in 37% yield. The presence of toluene as a ligand was a consequence of the treatment used for removing the zinc. After reduction of the volume of toluene solvent and chromatography on alumina with diethyl ether, $Ru(acac)_3$ (**25**)[28] was isolated in a 17% yield, as a result of the desilylation and isomerization of **20**. There was also ^1H NMR spectroscopy evidence of $(Cp^*)_2Ru$ (**26**)[2] as well as a small amount of brown powder, which may be $RuCl_3$.

The reaction of **2** with the lithium salt **21**, in the presence of EtOH and zinc, afforded $[Cp^*Ru(\eta^6\text{-}C_6H_6)]Cl$ (**27**)[18] as a yellow solid after treating the reaction mixture with benzene. Aromatic or chlorinated solvents should thus be avoided during the purification processes due to the favorability of arene and chlorine coordination by the Cp*Ru fragment. According to the previous results, the use of lithium salts **21** with **1** in THF offers a better synthetic alternative for the preparation of η^5-derivatives than the corresponding synthesis using **20** directly. However, the synthetic procedures could still be improved.

The ^{13}C NMR spectrum of **22** showed, at 132.2 ppm, the delocalized CO fragment of the oxopentadienyl ligand as well as the quaternary Cp* resonance (87.4 ppm). The assignment is consistent with those of similar molecules previously reported.[13,15,17,20,26] The ^{29}Si NMR spectroscopy showed a signal at 18.75 for the Me_3SiO substituent. Mass spectrometry at 20 eV gave evidence of the molecular ion at 408 (67%). Compound **23** showed typical ^1H and ^{13}C chemical shifts for such a coordinated substituted butadiene. Compounds **24**,[18] **25**,[28] **26**,[2] and **27**[18] could also be compared favorably with previously reported data in the literature.

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Structural Studies

Compounds **5**, **9**, **12**, and **15** have been further characterized by X-ray diffraction studies. Crystal data of ruthenium compounds are provided in Table 3.

***η^3*-Allyl Compounds $[Cp^*Ru(\eta^3\text{-}CH_2CHCHCHO)Cl_2]$ (5) $Cp^*Ru\{\eta^3\text{-}CH_2C(Me)CHC(Me)O\}Cl_2$ (9), and $Cp^*Ru\{\eta^3\text{-}CH(Me)CHCHOEt\}Cl_2$ (12).** Crystals for **5** and **9** were obtained from $CHCl_3$/hexane at −5 °C, except for **12**, which was crystallized at −15 °C. One molecule of $CHCl_3$ cocrystallized with compound **9**. The molecular structures for compounds **5**, **9**, and **12** are depicted in Figures 1, 2, and 3, respectively. Selected bond distances and angles are described in Table 4.

The solid state ruthenium(IV) structures contained an allylic fragment that adopted an *endo* conformation with respect to the Cp* ligand; the same conformation was generally found in solution, except for **9** (*vide supra*), in agreement with previous reports of related compounds and with the d^4 configuration of the ruthenium atom.[9,10,15,29,30]

The C−C bond distances within the allylic moiety are in good agreement with expectations for delocalized sp^2-carbon atoms bonded to ruthenium. The enyl ligand is bonded asymmetrically to the metal center, as has been observed for other substituted η^3-allyl complexes. In compound **5** the distance of Ru to the central carbon (C2) was shorter than that corresponding to carbons C(1) and C(3), as observed in many *endo*-allyl complexes, while **9** showed similar distances for the corresponding central and terminal carbon atoms. In the case of $Cp^*Ru\{\eta^3\text{-}CH(Me)CHCHOEt\}Cl_2$ (**12**), the corresponding terminal Ru−C bond distances were markedly different, being 2.207(4) Å for Ru−C2, but much longer at 2.410(4) Å for Ru−C4, which suggested preferential reactivity of C4 in presence of a nucleophile. The Ru−C allyl bond distances are reasonable, being on the order of 2.1−2.2 Å.[31,32]

Molecules of **12** were connected through C4−H4···Cl1 intermolecular interactions according to the crystal structure, which can be considered as weak hydrogen bonds since there is a H···Cl contact of 2.821 Å and a bond angle of 136.4° for C4−H4···Cl1. This interaction is responsible for the lengthening of the Ru−C4 bond distance.

The C−O bond lengths of 1.224(5) for **5**, 1.208(4) for **9**, and 1.340(4) Å for **12** were typical for uncoordinated aldehyde, ketones, or ether groups, as appropriate. The Ru−Cp* centroid distance for compound **9** (1.889 Å) was slightly longer than that for the less substituted complex **5** (1.881 Å), while the shortest distance was observed for the acetal derivative **12** (1.864 Å).

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Table 3. Crystal Data for Ruthenium Compounds 5, 9, 12, and 15

	5	9	12	15
formula	$C_{14}H_{20}Cl_2ORu$	$C_{16}H_{24}Cl_2ORu \cdot CHCl_3$	$C_{16}H_{26}Cl_2ORu$	$C_{32}H_{48}Cl_2O_2Ru_2Zn$
fw	376.27	523.69	406.34	803.11
cryst syst	monoclinic	orthorombic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_12_12_1$	$P2_1/c$	$P2_1/n$
a (Å)	13.7754(3)	12.1959(2) Å	8.5370(2)	11.1088(3)
b (Å)	7.8055(2)	12.9449(2)	13.8465(4)	13.1466(3)
c (Å)	14.5630(4)	13.4086(2)	14.5673(5)	23.2199(6)
$\alpha = \gamma$ (deg)	90	90	90	90
β (deg)	107.6680(1)	90	91.6630(10)	93.020(10)
V (Å^3)	1492.01(6)	2116.88(6)	1721.24(9)	3386.39 (15)
Z	4	4	4	4
cryst size (mm)	0.33 × 0.25 × 0.05	0.30 × 0.25 × 0.20	0.25 × 0.05 × 0.025	0.2 × 0.1 × 0.03
D_{calc} (g cm^{-3})	1.675	1.643	1.568	1.575
temp (K)	203(2)	203(2)	203(2)	223(2)
2θ scan range (deg)	7.14−54.98	6.84−54.96	7.26−54.96	6.98−55.02
index ranges	$-17 \le h \le 17$	$-15 \le h \le 15$	$-11 \le h \le 10$	$-14 \le h \le 13$
	$-9 \le k \le 10$	$-16 \le k \le 13$	$-17 \le k \le 17$	$-15 \le k \le 16$
	$-18 \le l \le 17$	$-17 \le l \le 17$	$-17 \le l \le 18$	$-30 \le l \le 29$
no. of rflns collcd	15 123	21 230	20 149	35 960
no. of indpt reflns	3385	4809	3922	7720
	$R_{int} = 0.0440$	$R_{int} = 0.0460$	$R_{int} = 0.0882$	$R_{int} = 0.1291$
final R1	0.0293	0.0275	0.0396	0.0497
final wR2	0.0673	0.0595	0.0763	0.0933
GOF	1.002	1.053	1.022	0.978
min./max. resid density/e Å^{-3}	−0.624, 0.640	−0.568, 0.386	−0.515, 0.801	−0.757, 0.721

The Ru−Cl bond distances in **5** and **9** [average: 2.4097(7) and 2.4057(7) Å, respectively] were found to be similar to those of other Ru(IV) complexes, such as [Cp*Ru(*endo*-C_3H_5)Cl_2], 2.408 Å;[30b] [CpRu(η^3-C_4H_4OMe)Cl_2], 2.403(1) Å;[30c] and [Cp*Ru{η^3-$CH_2C(Me)CHC(Me)O$}($SnCl_3$)(Cl)], 2.4002(9) Å,[15] while **12** [average 2.4235(9) Å] showed the longest Ru−Cl bond distances.

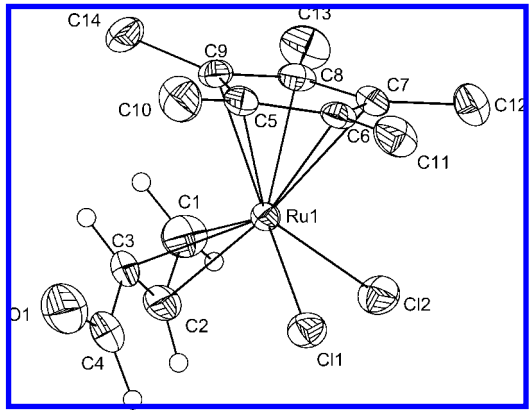


Figure 1. Crystal structure of [Cp*Ru(η^3-*endo-syn*-$CH_2CHCHCHO)Cl_2$] (**5**). Cp* hydrogen atoms have been omitted for clarity.

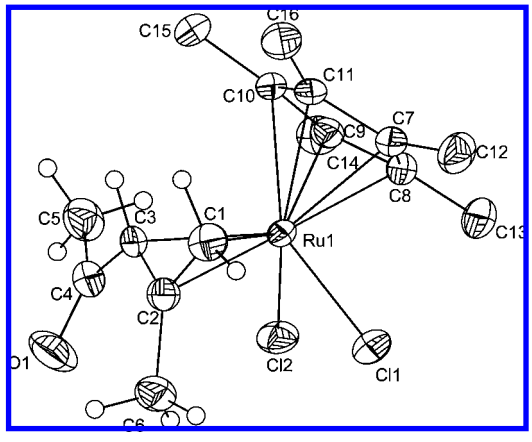


Figure 2. Crystal structure of [Cp*Ru{η^3-*endo-syn*-$CH_2C(Me)CHC(Me)O$}Cl_2] (**9**). Cp* hydrogen atoms have been omitted for clarity.

Compound Cp*Ru[η^5-$CH_2C(Me)CHC(Me)O]_2(\mu_2$-$ZnCl_2$) (15). The solid state structure of the oxopentadienyl compound **15** is presented in Figure 4, and bonding parameters are given in Table 5. Compound **15** has two half-open sandwich molecules bridged through a zinc dichloride unit via zinc−oxygen bonds. The zinc centers adopt a distorted tetrahedral geometry with O1, O2, Cl1, and Cl2 occupying the four coordination sites. The O1−Zn1−O2 angle [92.30(16)°] is similar to those of $[Zn(acac)_2]_3$ [∼90°][33] and $[Zn(acac)_2 \cdot H_2O]$ [∼90°].[34a] The O(1)−Zn(1) and O(2)−Zn(1) bond distances [1.997(4) and 2.003(4) Å, respectively] are typical for O−Zn(II) bonding, such as observed for $[Zn(acac)_2]$ [1.999(3) Å][33,34b] and $[Zn(acac)_2 \cdot H_2O]$ [2.02(2) Å],[34a] but longer than in gaseous $[Zn(acac)_2]$ [Zn−O, 1.942(6) Å].[34b]

The C1−C4 distances average 1.416(8) Å for the oxodienyl ligand, longer than that of the monometallic relative **8** [1.389(14) Å];[15] however, the C4−O1 bond distance [1.329(6) Å] was shorter than the corresponding value of 1.348(7) Å in compound **8**.

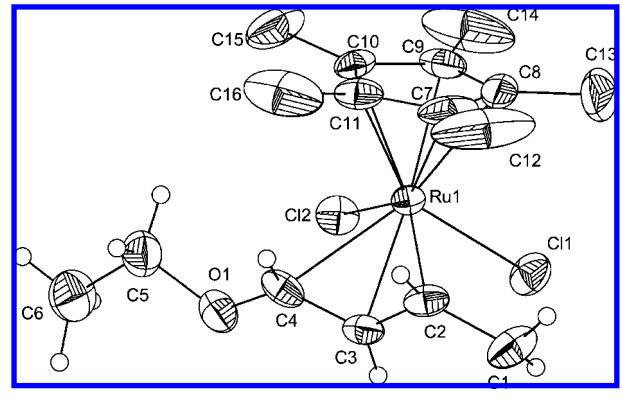


Figure 3. Crystal structure of [Cp*Ru{η^3-*endo-syn*-$CH(Me)CHCHOEt$}Cl_2] (**12**). Cp* hydrogen atoms have been omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) of Compounds 5, 9, and 12

bond lengths				bond angles			
	5	**9**	**12**		**5**	**9**	**12**
C1−C2	1.406(5)	1.417(4)	1.503(5)	C1−C2−C3	116.3(3)	111.6(3)	124.8(4)
C2−C3	1.414(5)	1.419(4)	1.407(6)	C2−C3−C4	120.5(3)	123.6(3)	117.1(4)
C3−C4	1.472(5)	1.497(4)	1.370(6)	O1−C4−C3	123.1(4)	122.1(3)	121.8(4)
C4−O1	1.224(5)	1.208(4)	1.340(4)	C2−C1−Ru1	68.68(18)	71.46(17)	
C1−Ru1	2.196(3)	2.187(3)		C4−C3−Ru1	120.0(2)		82.4(2)
C2−Ru1	2.134(3)	2.196(3)	2.207(4)	Cl1−Ru1−Cl2	83.64(3)	83.03(3)	83.33(4)
C3−Ru1	2.211(3)	2.238(3)	2.172(4)	C1−Ru1−Cl1	128.27(10)	82.45(9)	
Cl1−Ru1	2.4135(7)	2.4120(7)	2.4326(10)	C4−O1−C5			114.5 (3)
Cl2−Ru1	2.4059(8)	2.3994(7)	2.4139(9)	O1−C5−C6			107.2(4)
C4−C5		1.497(4)		C3−Ru1−Cl1	83.56(10)	123.45(8)	87.35(11)
C5−Si				O1−C4−C5		121.2(3)	
C7−Ru1	2.291(3)	2.223(3)	2.238(4)	C2−Ru1−C3	37.92(14)	37.32(11)	37.48(15)
C8−Ru1	2.202(3)	2.188(3)	2.213(4)	C1−Ru1−C3	65.84(15)	63.99(12)	
C9−Ru1	2.196(3)	2.252(3)	2.190(4)	C1−Ru1−C10		104.51(12)	
C10−Ru1		2.294(3)	2.213(4)	C3−C4−C5		116.6(3)	
C11−Ru1		2.278(3)	2.232(4)	C4−C5−Si1			
C12−Ru1				C1−Ru1−Cl2	81.17(11)	126.79(9)	
C13−Ru1				C2−Ru1−C7	157.99(13)	138.55(11)	81.45(16)
C4−Ru1			2.410(4)	C8−Ru1−C4			147.06(18)
C5−O1			1.449(5)	C2−Ru1−Cl1	93.11(10)	88.74(8)	85.08(11)
C5−C6			1.492(6)	C1−C2−Ru1	73.45(18)	70.82(16)	124.2(3)
C2−C6		1.500(4)		C3−C2−Ru1	73.98(18)	72.95(15)	69.9(2)
				C2−Ru1−Cl2	89.21(10)	91.18(8)	128.57(11)

Also, the average value for the Ru1−C(1−4) bonds [2.188(6) Å] was longer than that for compound **8** [2.168 (8) Å],[15] while the bond lengths Ru1−O1 [2.169(3) Å] and Ru2−O2 [2.165(3) Å] were quite similar to that of **8** [Ru1−O1, 2.167(5) Å]. The Ru−Cp* centroid distances of compound **15** (1.798 and 1.803 Å) were shorter than those of allyl compounds **5**, **9**, and **12** (*vide supra*) and similar to **8** (1.800 Å).

Discussion of Results and Comments

It has been possible to derive a comparative relationship of the chemical reactivity of compounds **1** and **2** with **3**, in which the influence of the solvent and the oxidation state of the precursors have been found to play important roles. The

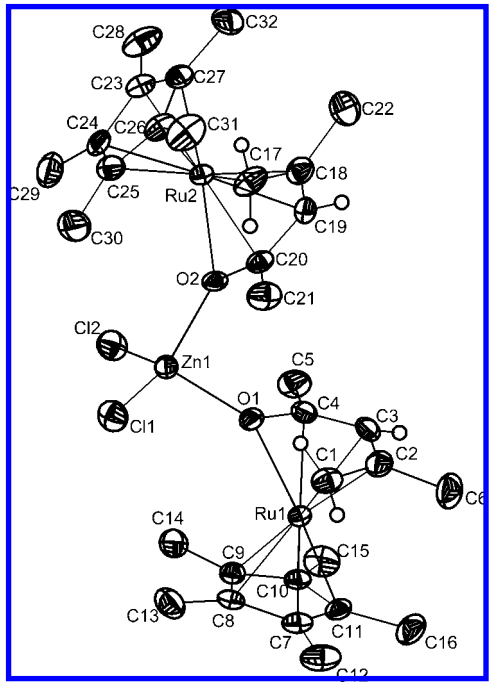


Figure 4. Crystal structure of [Cp*Ru[η^5-$CH_2C(Me)CHC(Me)O]_2$(μ_2-$ZnCl_2$)] (**15**). Hydrogen atoms of methyl groups have been omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) of Compound 15

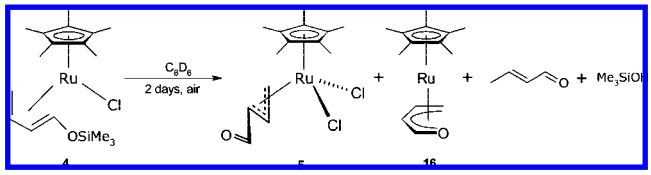
bond lengths		bond angles	
C(1)−C(2)	1.407(8)	C(1)−C(2)−C(3)	122.8(5)
C(2)−C(3)	1.425(8)	C(2)−C(3)−C(4)	125.2(5)
C(3)−C(4)	1.418(7)	O(1)−C(4)−C(3)	117.3(5)
C(4)−O(1)	1.329(6)	Zn(1)−O(1)−C(4)	130.5(3)
O(1)−Zn(1)	1.998(3)	C(17)−C(18)−C(19)	121.8(5)
O(2)−Zn(1)	2.004(3)	C(18)−C(19)−C(20)	125.4(5)
C(17)−C(18)	1.394(8)	Zn(1)−O(2)−C(20)	134.0(3)
C(18)−C(19)	1.419(8)	O(1)−Zn(1)−Cl(1)	102.67(11)
C(19)−C(20)	1.412(7)	O(1)−Zn(1)−Cl(2)	118.56(13)
C(20)−O(2)	1.332(6)	O(2)−Zn(1)−Cl(1)	119.00(12)
C(1)−Ru(1)	2.177(6)	O(2)−Zn(1)−Cl(2)	102.28(11)
C(2)−Ru(1)	2.191(6)	O(1)−Zn(1)−O(2)	92.43(14)
C(3)−Ru(1)	2.207(5)	Cl(1)−Zn(1)−Cl(2)	119.47(6)
C(4)−Ru(1)	2.178(5)	Zn(1)−O(1)−Ru(1)	147.83(18)
O(1)−Ru(1)	2.169(3)	Zn(1)−O(2)−Ru(2)	144.04(17)
C(17)−Ru(2)	2.164(6)	C(1)−Ru(1)−C(4)	87.4(2)
C(18)−Ru(2)	2.199(5)	C(1)−Ru(1)−O(1)	75.94(19)
C(19)−Ru(2)	2.201(5)	C(1)−Ru(1)−C(9)	149.3(2)
C(20)−Ru(2)	2.172(5)	C(17)−Ru(2)−C(20)	86.6(2)
Ru(2)−O(2)	2.165(3)	C(17)−Ru(2)−O(2)	75.6(2)

chemistry of the lower valent compound **1** showed basically selective reactions, while compound **2** was extremely reactive independent of solvent and substrate, resulting in less selective reactions. Compound **2** in THF afforded Ru(II) and Ru(IV) compounds **4** and **5**, respectively, while in the presence of alcohols, it afforded exclusively Ru(IV) compounds **9** and **10**−**13**, the latter being a consequence of nucleophilic attacks by MeOH or EtOH (Scheme 3).

Compound **4** was prepared in good yield from compound **1** and the corresponding ligand **3**. **4** suffered oxidative addition in the presence of $CDCl_3$ or $CHCl_3$ to give the corresponding Ru(IV) complex **5** and also afforded deep green trinuclear compounds, tentatively described as [$(Cp^*RuCl)_3Cl$]Cl and [$(Cp^*RuCl)_3CH$]Cl, the latter having been previously observed in similar systems.[15,35] Additionally, ^1H NMR spectroscopic data evidenced the liberation of crotonaldehyde.

Traces of ethanol in $CHCl_3$ were enough to transform compound **5** into the acetal **12**. The influence of the solvent followed according to the previous observations; moreover, in C_6D_6 in the presence of oxygen there was evidence of the

Scheme 6



disproportionation of compound **4** into **5** and **16**, accompanied by the release of crotonaldehyde and trimethylsilanol (Scheme 6).

However, in the absence of oxygen, the Cp*Ru fragment prefered to be coordinated by the arene to give [Cp*Ru(η^6-C_6D_6)]Cl, which showed that the ligand **3** could easily decoordinate and desilylate, as observed through the ^{1}H and ^{29}Si NMR spectroscopy, through which crotonaldehyde, Me_3SiOH, and Me_3SiOMe_3 were also detected.

Interestingly, the chemistry with ligands involving methyl groups as substituents, such as **6a** and **6b**, showed the opposite selectivity in the case of compounds **1** and **2**. Compound **1** showed no selectivity, giving **7**−**9**, and compound **2** afforded, in the presence or absence of a reducing reagent, **15** along with traces of **18** and **9**, respectively. Compound **9** could be obtained in a higher yield with this procedure, rather than with the one previously described,[15] and the *exo-syn* orientation was observed in the oxodienyl ligand in solution, whereas in the solid state the *endo-syn* conformation was obtained (*vide supra*).

It has been confirmed that the lithium salts of the anions resulting from deprotonation of α,β-unsaturated ketones,[15] such as **21**, are useful precursors in the synthesis of η^5-oxopentadienyl compounds. The presence of the trimethylsililoxy group as substituent in compounds **7**, **22**, and **23** was favored in the η^5-pentadienyl (**7**) and η^5-oxopentadienyl (**22**) complexes, compared to the results observed for η^4-butadiene complex **23** due to the instability of the latter under chromatographic conditions. The ketone ligand **20** was not a good source of oxopentadienyl ligands because of its preference to isomerize in the presence of ruthenium, which provided acac ligands, leading to Ru(acac)$_3$ (**25**).

It is relevant to mention that there are many synthetic procedures reported that use compound **2** as starting material. However, in most reports there is no consideration or discussion about the high reactivity of this complex on exposure to traces of nucleophiles, such as oxygen, water, alcohols, arenes, and chlorinated compounds, among others. From these studies it is now clear that the selection of the solvent is crucial, as are other factors such as the purity of the starting materials, an inert atmosphere, and the aging of the Cp*RuCl species. All this will determine the possible products that should be considered to be present in a product mixture. The study of this chemistry has allowed us to isolate diverse and interesting compounds, some of them even having been previously obtained by different routes, which allowed the establishment of the relative stabilities of analogous species, as well as general trends of Cp*Ru(oxopentadienyl) chemistry.

Experimental Section

General Remarks. All experiments were carried out under a nitrogen or argon atmosphere 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_6D_6, and CD_3COCD_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 Desert Analytics, Tucson, AZ. Mass spectra were obtained with a Hewlett-Packard HP-5990A. Ionization was by FAB with xenon atoms at 6 keV energy (Washington University, St. Louis, MO). Reagents $RuCl_3 \cdot 3H_2O$, buta-1,3-dienyloxytrimethylsilane, 4-trimethylsiloxy-3-penten-2-one (**20**), and zinc were purchased from Aldrich and Strem, respectively; aluminum oxide (activated neutral Brockman I) and silica gel (Merck, 0.04−0.063) were used as received. The (Cp*RuCl)$_4$ (**1**)[8,19] and (Cp*RuCl$_2$)$_2$ (**2**)[3a] reagents were synthesized using literature procedures.

Synthesis of [Cp*Ru(η^4-CH$_2$CHCHCHOSiMe$_3$)Cl] (4). A solution of **1** (300 mg, 1.1 mmol) in 25 mL of THF at −110 °C was added dropwise to 0.19 mL (1.1 mmol) of **3**. The solution was stirred with slow warming to room temperature, and after stirring for 1 h, the reaction mixture was filtered and the volatiles were removed under vacuum. Compound **4** was then extracted from the remaining residue with hexane (50 mL), and the solution was concentrated and cooled to −5 °C, which resulted in the formation of light orange needles (400 mg, 0.96 mmol, 88% yield). Mp: 103−105 °C. Anal. Calcd for $C_{17}H_{29}ClOSiRu$: C, 49.33; H, 7.01, Si, 6.77. Found: C, 49.53; H, 7.02; Si, 7.02. IR (KBr, cm^{-1}): 2956 (m), 2910 (m), 1654 (m, br), 1250 (s), 1170 (vs), 872 (vs), 848 (s). LR FAB MS (matrix: 3-NBA/Li): *m*/*z* 414 (40) [M$^+$], 379 (100), 364 (88).

Synthesis of [Cp*Ru(η^4-CH$_2$CHCHCHOSiMe$_3$)Cl] (4) and [Cp*Ru(η^3-CH$_2$CHCHCHO)Cl$_2$] (5).[20] Compound **3** (0.37 mL, 2.1 mmol) in THF (2 mL) at room temperature was added to a brown-red solution that contained 650 mg (2.1 mmol) of compound **2** in 25 mL of THF. After the mixture was stirred for 1 h, it turned yellow-brown; 30 min later, the solvent was filtered and evaporated under reduced pressure to afford an orange-red residue. Compound **4** was extracted with hexane (60 mL), resulting in a 40% yield (350 mg, 0.85 mmol).

The mustard yellow residue that was insoluble in hexane was dissolved in acetone (2 mL) and purified on a silica gel chromatographic plate. Compound **5** eluted with a mixture of ethyl acetate/acetone (8:2) as an orange band, which was extracted with acetone. This fraction was crystallized from $CHCl_3$/hexane. Compound **5** was obtained as orange-red crystals in 56% yield (442 mg, 1.18 mmol), without melting or decomposing until over 200 °C. Anal. Calcd for $C_{14}H_{20}Cl_2ORu$: C, 44.68; H, 5.30. Found: C 44.52, H 5.37. IR (KBr) cm^{-1}: 2968 (m), 2915 (m), 2861 (m), 1691 (vs), 1479 (m). LR-FAB MS (matrix: 3-NBA/Li): *m*/*z* 382 (70) [M$^+$+Li], 383 (100) [M$^+$+1+Li].

Syntheses of Compounds CH$_2$C(Me)CHC(Me)OSiMe$_3$ (6a) and CH$_3$C(Me)C(OSiMe$_3$)CHCH$_2$ (6b). The syntheses of **6a** and **6b** have already been published, but from different synthetic procedures.[36]

n-BuLi (8.9 mL, 1.6 M, 14.3 mmol) was added to a solution of diisopropylamine (2.00 mL, 14.3 mmol) in 15 mL of THF at −78 °C. The solution was stirred with slow warming to room temperature. After 15 min, the solution was cooled at −78 °C and mesityl oxide (1.60 mL, 14.3 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred for 1 h, then Me_3SiCl (1.81 mL, 14.3 mmol) was added to the light yellow solution at −78 °C. Afterward, the cold bath was removed and the solution was warmed to room temperature, giving a colorless

(33) Bennett, M. J.; Cotton, F. A.; Eiss, R. *Acta Crystallogr. Sect. B* **1968**, *24*, 904.
(34) (a) Montgomery, H.; Lingafelter, E. C. *Acta Crystallogr. Sect. B* **1963**, *16*, 748. (b) Shibata, S.; Ohta, M. *J. Mol. Struct.* **1981**, *77*, 265.
(35) (a) Kakigano, T.; Suzuki, H.; Igarashi, M.; Moro-oka, Y. *Organometallics* **1990**, *9*, 2192. (b) Rondon, D.; Delbeau, J.; He, X.-D.; Sabo-Etienne, S.; Chaudret, B. *J. Chem. Soc., Dalton Trans.* **1994**, 1895.
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solution. The volume of the solvent was reduced (~5 mL), hexane (40 mL) was added, and the LiCl was filtered. The supernatant was evaporated, and the yellow oil was distilled in a horizontal distillation apparatus[37] under reduced pressure (0.075 mmHg). The products distilled as a colorless liquid at 30−32 °C, in 79% yield (191 g, 1.13 mmol). This mixture of isomers was used for subsequent reactions.

Syntheses of Compounds [Cp*Ru{η^5-$CH_2C(Me)CHC(OSiMe_3)CH_2$}] (7), [Cp*Ru($\eta^5$-$CH_2C(Me)CHC(Me)O$] (8),[13,15] and [Cp*Ru{η^3-$CH_2C(Me)CHC(Me)O$}]Cl_2] (9).[15] Identification of Compound [$(C_5Me_4CHO)Ru\{\eta^5$-$CH_2C(Me)CHC(Me)O\}$].[15] A mixture of compounds **6a** and **6b** (410 mg, 2.40 mmol), in 2 mL of THF, at room temperature was added to a solution of **1** (370 mg, 1.36 mmol) in THF (15 mL). The yellow-brown solution was stirred for 3 h. After filtration, the solvent was evaporated to dryness and the remaining brown-red residue was extracted with diethyl ether (3 × 5 mL); then the solvent was concentrated and the solution was purified on a column (2.5 × 16 cm) of alumina. This solution was subsequently eluted from hexane/diethyl ether (9:1) to remove compound **7**, then from diethyl ether to afford compound **8**, and finally from acetone to give $(C_5Me_4CHO)Ru\{\eta^5$-$CH_2C(Me)CHC(Me)CO\}$.[15] Compound **7** was purified again by chromatography on alumina (2.5 × 8 cm) with elution by diethyl ether, yielding a yellow powder (11 mg, 0.027 mmol) in 2% yield, melting point 80−83 °C. Compound **8** was obtained as yellow crystals at −5 °C, which were precipitated from diethyl ether, in 20% yield (90 mg, 0.22 mmol). Mp: 90−92 °C.

The brown-red fraction, which was insoluble in diethyl ether, was recrystallized from acetone/diethyl ether to afford **9**. This compound was obtained as a brown-red powder and was purified by thin-layer chromatography, using silica gel and acetone as eluent. An orange band was separated and extracted with acetone; after reducing its volume to ~2 mL and adding hexane, compound **9** was obtained as red-orange crystals at −5 °C, in 17% yield (95 mg, 0.23 mmol). This compound did not melt until at least 200 °C.

Synthesis of Compound [Cp*Ru{η^3-$CH_2C(Me)CHC(Me)O$}]Cl_2] (9).[15] To compounds **6a** and **6b** (175 mg, 1.02 mmol) at room temperature was added 240 mg (0.78 mmol) of **2** in 15 mL of EtOH. The brown solution turned yellow-green. The mixture was stirred at room temperature for 6 h. The yellow-brown solution was filtered and evaporated under vacuum. The brown residue was redissolved in 4 mL of CH_2Cl_2, and 15 mL of hexane was added, affording a red-brown powder at −5 °C, which was purified by thin-layer chromatography, using silica gel and acetone as eluent. Red-orange needles of *endo-syn*-**9** suitable for X-ray analysis were deposited after slow diffusion of $CHCl_3$/hexane, in 25% yield (79 mg, 0.20 mmol).

Syntheses of [Cp*Ru(η^3-$CH_2CHCHCHO$)Cl_2] (5), [Cp*Ru{η^3-*endo*-CH(Me)CHCHOMe}]Cl_2 (10), and [Cp*Ru{η^3-*endo*-$CH_2CHCHCH(OMe)_2$}]Cl_2] (11). Compound **3** (0.15 mL, 0.85 mmol) was added to a cold solution (−110 °C) of **2** (200 mg, 0.65 mmol) in methanol (30 mL). The reaction mixture was warmed to room temperature and stirred for 4 h. The brown solution turned yellow-brown. After filtration, the solvent was removed under vacuum. Addition of diethyl ether to the red-brown residue gave an orange-red solution, which was evaporated and dissolved in $CHCl_3$; this solution was transferred to a chromatography column packed with Al_2O_3. A yellow band could be eluted with $CHCl_3$, which was collected, reduced in volume, and diluted with hexane. Compound **11** was obtained at −5 °C as orange-yellow needles with a melting point of 150−160 °C, in 8% yield (22 mg, 0.052 mmol). The residue, insoluble in diethyl ether, was extracted with toluene; the solution was concentrated, and the red product was purified on a preparative silica gel plate, using acetone. An orange band was eluted from ethyl acetate/acetone (8:2); the residue, after evaporation, was extracted with acetone. Compound **5** was obtained as orange-red needles from $CHCl_3$/hexane, in 37% yield (91 mg, 0.24 mmol). Compound **11**: Anal. Calcd for $C_{16}H_{26}Ru_1Cl_2O_2$ C, 45.49; H, 6.20. Found: C, 44.98; H, 6.10. IR (KBr, cm^{-1}): 2973 (m), 2911 (s), 1691 (m, br), 1537 (s), 1459 (s, br), 1378 (s), 1291 (s), 1229 (vs), 1093 (s), 1029 (vs), 855 (s), 462 (m). MS: *m*/*z* 236 (100), 277 (31), 305 (11), 350 (8), 377 (14), 466 (4).

Compound **10** was obtained from the yellow residue, which was insoluble in diethyl ether and toluene. This yellow powder was crystallized from $CHCl_3$ and hexane at −15 °C; **10** precipitated as an orange-yellow powder, in 13% yield (33 mg, 0.08 mmol), which did not melt or decompose until at least 200 °C. Anal. Calcd for $C_{15}H_{24}Cl_2ORu$: C, 45.92; H, 6.16. Found: C, 44.98; H, 6.09. IR (KBr, cm^{-1}): 2989 (m), 1261 (m), 1214 (vs), 1097 (m), 1018 (m), 807 (m). LR-FAB MS (matrix: 3-NBA/Li): *m*/*z* 399 (100) [M^++Li], 401 (95) [M^++1+Li].

Synthesis of [Cp*Ru(η^3-$CH_2CHCHCHO$)Cl_2] (5), [Cp*Ru{η^3-*endo*-CH(Me)CHCHOEt}Cl_2] (12), and [Cp*Ru{η^3-*endo*-$CH_2CHCHCH(OEt)_2$}Cl_2] (13). (a) Reaction at Room Temperature in a 1:1 Ratio. Compound **2** (483 mg, 1.57 mmol) was dissolved in 30 mL of EtOH and cooled to −110 °C, after which 0.27 mL (1.57 mmol) of **3** was added dropwise to the cold, stirred solution. After the solution was slowly warmed to room temperature, a brown-yellow solution was formed. The mixture was stirred at room temperature for 7 h, the solvent was removed under vacuum, and the residue was extracted with three portions (6 mL) of toluene. The toluene solution was evaporated, and the orange-red residue was dissolved with a mixture of acetone/ethyl acetate (1:1) and chromatographed over Al_2O_3 (20 × 2 cm). The first (yellow) band was collected with ethyl acetate. After the evaporation of the solvent, the residue was recrystallized from toluene/pentane at −5 °C, yielding **13** as yellow-orange needles (191 mg, 0.42 mmol, 27%). Mp: 159−162 °C. A second band was eluted with acetone/ethyl acetate (1:1). After the evaporation of the solvents and the recrystallization from $CHCl_3$/hexane at −5 °C, it gave compound **12** as yellow needles with mp 169−171 °C in 5% yield (32 mg, 0.078 mmol). The residue, not soluble in toluene, was dissolved in acetone and purified on a preparative silica-gel plate. The eluent was a mixture of acetone/ethyl acetate (8:2). The orange band was removed and extracted with acetone from the silica. Compound **5** was obtained as an orange-red powder, which, after recrystallization from $CHCl_3$/hexane at −15 °C, produced orange-red needles in 15% yield (90 mg, 0.24 mmol). Compound **12**: Anal. Calcd for $C_{16}H_{26}Cl_2ORu \cdot H_2O$: C, 45.28; H, 6.65. Found: C, 45.17; H, 6.63. IR (KBr, cm^{-1}): 2982 (m), 2908 (m), 1538 (s), 1452 (m, br), 1380 (vs), 1217 (s), 1094 (s), 1030 (s), 853 (m, br). Compound **13**: Anal. Calcd for $C_{18}H_{30}Ru_1Cl_2O_2$: C 47.99, H 6.71. Found: C 47.71, H 6.90. IR (KBr, cm^{-1}): 2976 (s), 2918 (s), 1693 (m), 1482 (m, br), 1446 (m, br), 1381 (m), 1117 (s), 1080 (s), 1051 (vs), 1019 (s), 992 (vs). MS: *m*/*z* (20 eV): 236 (100), 277 (31), 305 (11), 350 (8), 377 (14.1).

(b) Reaction at Room Temperature in a 1:3 Ratio. To a cold solution (−110 °C) of **2** (358 mg, 1.16 mmol) in 30 mL of EtOH was added 0.61 mL (3.48 mmol) of **3**. The solution was stirred 15 h at room temperature. After the filtration and removal of the solvent, a red residue was obtained and extracted with toluene (10 mL). The red solution was evaporated, and the residue was dissolved with acetone and purified on a preparative silica gel plate. The orange band was eluted with a mixture of acetone/ethyl acetate (8:2). After the evaporation and the extraction of acetone, compound **5** was obtained as orange-red needles in 57% yield by recrystallization from $CHCl_3$/hexane (250 mg, 0.66 mmol). The mustard-yellow residue, not soluble in toluene, was passed through a chromatography column (2 × 25 cm) packed with silica-gel. A yellow-orange band could be eluted with diethyl ether. Evaporation

(37) Gutiérrez, J. A. *J. Chem. Educ.* **2001**, *78*, 653.

of the solvent and recrystallization from $CHCl_3$/hexane at −15 °C gave compound **12** as an orange powder in 17% yield (80 mg, 0.19 mmol).

(c) Reaction Carried Out under EtOH Reflux. A 100 mL round-bottomed flask was charged with 500 mg (1.6 mmol) of **2**, 30 mL of EtOH, and 0.57 mL (3.2 mmol) of **3**. Refluxing the brown solution for 5 h resulted in a yellow-brown solution; after filtration the solvent was evaporated under vacuum. The dark orange residue was extracted with six 8 mL portions of toluene; traces of compound **5** were separated in this way. Compound **12**, not soluble in toluene, was obtained as orange needles in 48% yield (317 mg, 0.78 mmol) after recrystallization from $CHCl_3$/hexane. Mp: 169−171 °C.

Identification of Compounds [Cp*Ru(η^5-$CH_2CHCHCHO$)]$_2$(μ_2-$ZnCl_2$) (14), Cp*Ru(η^4-$CH_2CHCHCHOEt$)Cl (17), and Cp*Ru(η^5-$CH_2CHCHCHO$) (16). A solution of **2** (500 mg, 1.60 mmol) in 25 mL of EtOH to which zinc dust had been added (400 mg, 6.10 mmol) was stirred at room temperature for 5 min. Then, 0.30 mL (1.71 mmol) of **3** was added to the red-brown solution. The solution turned yellow-brown, and it was kept stirring for 1.5 h, after which the solvent was removed under vacuum. Compound **14** was extracted with diethyl ether (20 mL) and obtained as a yellow powder at −5 °C in 1.5% yield (9.00 mg, 0.024 mmol). The orange-brown residue was dissolved in a minimal volume of acetone and 20 mL of diethyl ether, leading to a yellow-brown oil, which settled out of the solution. The oil was dissolved in acetone and then transferred to a chromatography column packed with Al_2O_3. Compound **16** was obtained from the yellow fraction with diethyl ether and isolated as yellow needles in 12% yield (59 mg, 0.19 mmol). The supernatant liquid was placed at −15 °C, and a brown powder, a mixture of compounds **16** and traces of **17**, was formed.

Syntheses of Compounds [Cp*Ru{η^5-$CH_2C(Me)CHC(Me)O$}]$_2$(μ_2-$ZnCl_2$) (15) and Cp*Ru{η^4-$CH_2C(Me)CHC(Me)OH$}Cl (18). Zinc dust (600 mg, 9.18 mmol) at room temperature was added to an ethanol solution (20 mL) of **2** (500 mg, 1.63 mmol). The deep green solution was stirred 5 min, and afterward compounds **6a** and **6b** (340 mg, 1.97 mmol) were added. The solution turned brown-yellow and was stirred at room temperature for 6 h. Then, the zinc was removed by filtration and the solvent was evaporated. Compound **18** was then extracted from the residue with diethyl ether (10 mL), and the resulting yellow solution was concentrated. On cooling to −15 °C, **18** was obtained as a yellow powder (5.00 mg, 0.013 mmol).

The diethyl ether insoluble fraction was extracted with toluene (10 × 20 mL), which gave a yellow solution. After the solvent was concentrated and hexane (30 mL) was added, compound **15** was obtained as a yellow powder. Single canary-yellow crystals were obtained through the recrystallization from CH_2Cl_2/hexane at −15 °C, in 31% yield (202 mg, 0.25 mmol). Mp: 236−239 °C. Anal. Calcd for $C_{32}H_{48}Ru_2Cl_2O_2Zn$: C, 47.85 H, 5.99. Found: C, 47.66; H, 5.84. IR (KBr) cm^{-1}: 2911 (s), 1442 (mv), 1379 (s), 1340 (s), 1026 (s,b), 917 (s). MS: *m*/*z* 136(100), 236 (25), 289 (13), 334 (32).

Synthesis of Cp*Ru[η^5-$CH_2C(OSiMe_3)CHC(Me)O$] (22) and Identification of Cp*RuCl[η^4-$CH_2C(OSiMe_3)CHCMe(OH)$] (23). n-BuLi (0.5 mL, 1.6 M, 0.73 mmol) was added to a solution of diisopropylamine (100 μL, 0.73 mmol) in 1.5 mL of THF at −78 °C. The solution was stirred with slow warming to room temperature. After 15 min, the solution was cooled to −110 °C, and **20** (140 μL, 0.73 mmol), in 1 mL of THF, was added dropwise to afford [$CH_2C(OSiMe_3)CHC(Me)O$]Li (**21**). The reaction mixture was warmed to room temperature and stirred for 30 min, and then **21** was added, at −110 °C, to **1** (200 mg, 0.73 mmol); the dark brown solution gradually changed to a reddish-yellowish brown on warming to room temperature. The mixture was maintained for 1 h under stirring. After filtration, the solvent was evaporated and compounds **22** and **23** (1:0.1) were extracted, as a dark green solution, with hexane/diethyl ether (1:1). The solvent was evaporated and the green solid was sublimed at 70 °C and 0.5 mmHg during 4 h. The yellow-green oil was kept for 30 days at −78 °C, after which an olive green solid (240 mg) was isolated. The solid was a mixture of **22** (80%) and **23** (3%) according to ^{1}H NMR spectroscopy.

The mixture of **22** and **23** was subjected to chromatography on alumina (2 × 10 cm), from which two fractions were obtained. Two yellow fractions were obtained from hexane/diethyl ether (1:1) and diethyl ether, respectively. The first fraction was a mixture of **22** and another unknown species with chemical shifts as follows. ^{1}H NMR (C_6D_6): 1.71 (s, Me), 4.05 (t, J = 1.6 Hz, CH), 4.14 (t, J = 1.6 Hz, CH), 1.88 (s, Cp*). ^{13}C NMR: 13.8, (Me), 72.8 (CH), 74.5 (CH), 12.2 (Me, Cp*), 87.6 (C,Cp*). The second fraction was kept 7 days at − 5 °C, after which the diethyl ether was removed and compound **22** was isolated as ∼1 mL of a yellow liquid. IR (KBr) cm^{-1}: 2958 (s), 2911 (s), 1458 (s), 1382 (s), 1277 (s), 1247 (s), 1162 (s), 1014 (s,br), 993 (s), 947 (s), 846 (s,br). MS: *m*/*z* 408 (67), 326 (100), 311 (87), 292 (7), 233 (38), 206 (4).

Formation of [Cp*Ru(C_5H_5Me)]Cl (24),[18] [Ru(acac)$_3$] (25),[28] and Cp*$_2$Ru (26).[2] A solution of **2** (235 mg, 0.76 mmol) and zinc dust (100 mg, 1.5 mmol) in EtOH (25 mL) was stirred at room temperature for 5 min. Then, 145 μL (0.76 mmol) of **20** was added to the dark green solution already formed. After 22 h the solution turned red-brown with formation of a yellow-orange precipitate. This was filtered and the solid redissolved in 15 mL of toluene, in order to remove the excess of zinc. The solvent was reduced to ∼3 mL and addition of hexane (20 mL) afforded compound **24** as a cream-colored solid. Single colorless crystals were obtained through recrystallization from CH_2Cl_2/hexane at −78 °C, in 37% yield (103 mg, 0.28 mmol). Mp: 235−245 °C.

The red ethanolic solution was evaporated until dryness and the residue was extracted with ∼10 mL of toluene. Compound **25** was obtained after chromatography on an alumina column (2.5 × 8 cm), from which one pale pink fraction was obtained. **25** precipitated as wine needles at −15 °C, in 17% yield (52 mg, 0.13 mmol). Mp: 135−145 °C. ^{1}H NMR ($CDCl_3$): 1.63 (s, Me), 10.33 (br, H). There was spectroscopic evidence of the presence of **26** in the residue, through ^{1}H NMR spectroscopy, but it was not isolated.

Isolation of Compound 16 from Compound 4 from (a) Neutral Alumina. Compound **4** (220 mg, 0.53 mmol) was dissolved in hexane/diethyl ether (1:1) and gave a yellow solution, which was chromatographed on a neutral Al_2O_3 (2.5 × 20 cm) column with diethyl ether as the eluant. A yellow band was collected and the solvent was removed under vacuum; the yellow product was crystallized from pentane at −15 °C to give 100 mg (0.33 mmol, 62%) of **16**[20] as yellow crystals that melt at 92−93 °C.

(b) Deactivated Neutral Alumina. A hexane/diethyl ether (1:1) solution of **4** (200 mg, 0.48 mmol) was passed through a chromatography column (2.5 × 15 cm) packed with deactivated neutral Al_2O_3 (5% H_2O).[38] A yellow band was eluted from diethyl ether, collected, and reduced in volume. Yellow crystals of **16** crystallized at −15 °C in 67% yield (98.8 mg, 0.32 mmol).

(c) Florisil. This synthesis was carried out by a procedure similar to the one described for methods (**a**) and (**b**). Compound **4** (125 mg, 0.30 mmol) was dissolved in hexane/diethyl ether and chromatographed on a (2 × 8 cm) Florisil column with hexane/diethyl ether as eluent (1:1). The yellow band afforded **16** in 20% yield (18.5 mg, 0.06 mmol).

Reactivity of Compound 4 in C_6D_6 and C_6H_6. (a) Formation of [Cp*Ru(η^6-C_6H_6)]Cl (27). A yellow C_6H_6 solution (20 mL) of compound **4** (300 mg, 0.72 mmol) was refluxed, leading to a light orange solution. The solution turned dark brown after 12 h and a cream-colored solid precipitated. The solution was filtered

(38) Neutral alumina was deactivated like the procedure reported in: Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 119.

and a pale yellow solid was washed with diethyl ether (2 × 5 mL). Compound **27** was obtained as a pale yellow solid in 38% yield (97 mg, 0.27 mmol).[18,19]

(b) Formation of [Cp*Ru(η^6-C_6D_6)]Cl. Compound **4** (6 mg, 0.01 mmol) was dissolved in C_6D_6 (1 mL) and then transferred to a sealed NMR tube. Gradually the light yellow solution turned pale yellow. After 15 days a white powder precipitated. The solid was decanted, and the resulting ^{1}H and ^{13}C NMR spectra were in agreement with those of the cationic compound [Cp*Ru(η^6-C_6D_6)]Cl, analogous to **27**. The NMR chemical shifts showed a pair of signals for ^{1}H and ^{13}C at 2.03 (Cp*, s); 6.0 (C_6H_6, s) and 11.7 (Me, Cp*); 97.1 (C, Cp*), 87.8 (C_6H_6), respectively.

Reactivity of Compound 4 in $CDCl_3$. (a)Formation of Compounds 2, 5, and 12 and Tentative Identification of [(Cp*RuCl)$_3$Cl]Cl. A solution of **4** (172 mg, 0.41 mmol) in $CHCl_3$ (35 mL) was maintained under reflux for 12 h. After 5 min the orange-red solution had changed to dark brown, and then it became dark yellow-green. The solvent was reduced under vacuum and filtered through Celite. An orange solution, a mixture of compounds **5** and **12**, was obtained. Both complexes were separated on a silica gel plate with ethyl acetate/acetone (8:2). One orange band was extracted with acetone; then the solvent was evaporated and the resulting red-orange powder was crystallized from $CHCl_3$/hexane. Compound **5** precipitated as orange-red crystals, in 33% yield (51.7 mg, 0.14 mmol). Compound **12** was decomposed by means of this method, but in subsequent experiments it was purified on a chromatographic column (neutral alumina, 12 × 2 cm). A mixture of **12** and **5** was dissolved in a minimum volume of ethyl acetate/acetone (1:1); this afforded, after chromatography, one fraction with compound **12**, which was eluted with ethyl acetate. After recrystallization from $CHCl_3$/hexane, **12** was precipited as a yellow-orange powder in 10% yield (10 mg, 0.024 mmol). Compound **5** was retained on the chromatographic column.

The green residue that remained in the Celite was separated with CH_2Cl_2 and precipitated as a dark green powder from CH_2Cl_2/diethyl ether at −5 °C. This product was part of a mixture with compound **2** [NMR ($CDCl_3$): ^{1}H δ 4.83 (br)], and the new species is tentatively assigned as the trimetallic compound [(Cp*RuCl)$_3$Cl]$^+$ according to the spectroscopic data [NMR ($CDCl_3$): ^{1}H δ 1.85 (br); ^{13}C δ 13.4, 98.0 ppm].

(b) Formation of Compounds 5 and [(Cp*RuCl)$_3$CH]Cl. Compound **4** (120 mg, 0.28 mmol) in $CHCl_3$ (30 mL) without EtOH[39] was maintained under reflux for 6 h. The orange solution turned dark green. The $CHCl_3$ was removed under vacuum and acetone was added. The green solution was then purified by thin-layer chromatography on silica gel using acetone/ethyl acetate (8:2) as eluent. There were two bands: the orange band was separated and extracted with acetone, and after crystallization from acetone/hexane, compound **5** was obtained as orange-red crystals in 18% yield (20 mg, 0.05 mmol). The green band was extracted with EtOH, and after reducing the volume of the solvent (∼2 mL), the addition of hexane, and cooling at −15 °C, compound [(Cp*RuCl)$_3$CH]$^+$Cl was isolated as a green powder in 6% yield (15 mg, 0.017 mmol).[15,35]

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Supporting Information Available: X-ray crystallographic data for compounds **5**, **9**, **12**, and **15** and NMR spectra of compounds **17**, **18**, **22**, and **23**. This information is available free of charge via the Internet at http://pubs.acs.org.

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Article

Comparative Study of the Reactivity of (Cp*RuCl) and (Cp*RuCl) with Trimethylsilyl-Substituted Oxodienyl Ligands

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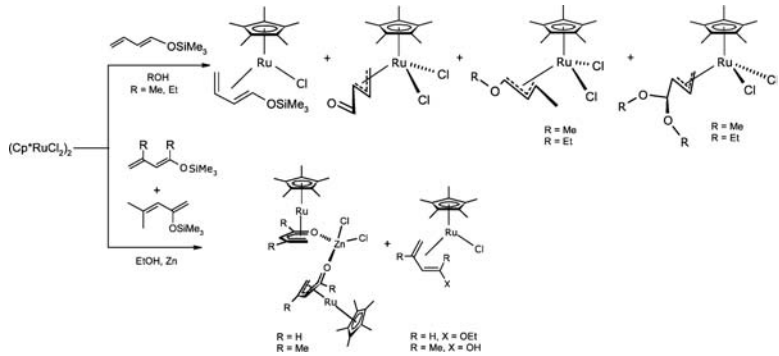

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