Articles

Syntheses, Structures, and Reactivity Studies of Half-Open Ruthenocenes and Their Oxodienyl Analogues

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Received August 10, 2001

Improved synthetic routes to Cp*Ru(Pdl) complexes (Pdl = 2,4-dimethylpentadienyl and various oxodienyl ligands) including Cp*Ru(η^5-2,4-Me_2-C_4H_3O) (**1**), Cp*Ru[η^5-2,4-(t-Bu)$_2$-C_4H_3O] (**1′**), and Cp*Ru(η^5-2,4-Me_2-C_5H_5) (**1″**) have been developed, and the relative reactivities of the resulting complexes toward oxidative addition or ligand addition reactions have been examined. Thus, the oxopentadienyl complexes **1** and **1′** and the 2,4-dimethylpentadienyl complex **1″** were found to undergo oxidative addition of $SnCl_4$, Me_2SnCl_2, I_2, Cl_2 (via $CHCl_3$), and O_2, yielding Cp*Ru[η^3-$CH_2C(R)CHC(R)O$](X_1)(X_2) [R = Me, X_1 = Cl, X_2 = $SnCl_3$ (**2**); R = Me, X_1 = X_2 = I (**3**); R = t-Bu, X_1 = X_2 = I, (**3′**); R = Me, X_1 = X_2 = Cl (**4**); R = t-Bu, X_1 = X_2 = Cl (**4′**)] or Cp*Ru[η^3-$CH_2C(Me)CHC(Me)CH_2$](X_1)(X_2) [(X_1) = Cl, (X_2) = $SnClMe_2$ (**2a″**); (X_1) = (X_2) = I_2 (**3″**); (X_1) = (X_2) = Cl_2 (**4″**)] and a peroxide Cp*Ru[η^3-$CH_2C(Me)CHC(Me)O$](O_2) (**5**) readily, the oxodienyl products having η^3-oxodienyl coordination occurring preferentially through an all-carbon allylic fragment, in line with ruthenium's soft nature. The O_2 reaction was of additional interest in that it also led to a product in which oxidation of the Cp* ligand to a C_5Me_4(CHO) ligand had occurred, giving (η^5-C_5Me_4-CHO)Ru[η^5-$CH_2C(Me)CHC(Me)O$] (**6**). In contrast to the above, reactions of the 2,4-di(*tert*-butyl)oxodienyl or 2,4-dimethylpentadienyl ligand complexes were much less favorable, occurring much more slowly, if at all. For the reaction of $CHCl_3$ with the 2,4-dimethylpentadienyl complex, a small amount of an η^6-toluene complex, [Cp*Ru(η^6-C_7H_8)][Cp*$RuCl_3$] (**11**), was formed, apparently as a result of a carbon−carbon bond activation, giving a rearrangement of the dienyl ligand. The additions of Lewis bases to the oxodienyl complexes, leading to Cp*Ru[η^3-$CH_2C(Me)CHC(Me)O$]L species [L = PPh_3 (**7**), $PHPh_2$ (**8**), PMe_3 (**9**), CO (**10**)], were most facile for small donors such as PMe_3, while PPh_3 and CO additions were more reversible. Structural data have been obtained for representative examples of the above, i.e., complexes **1**, **1′**, **2**, **5**, **6**, **7**, and **11**.

Introduction

Half-open ruthenocene complexes have proven to be quite versatile, as it has been found to be straightforward to incorporate into their pentadienyl ligands a wide variety of substituents, including alkyl, aryl, CF_3, and siloxy groups.[1] Additionally, it has also been possible to incorporate heteroatoms such as oxygen or nitrogen into the dienyl fragments. Thus, we have reported previously the syntheses of several η^4-aminopentadiene, η^3- and η^5-azapentadienyl, and η^5-oxopentadienyl ruthenium Cp* complexes.[1−3]

Because of the interesting chemistry displayed by the oxodienyl complexes, and especially their major differences relative to the simple dienyl[4] and azadienyl[2] complexes, it was of particular interest to study the reactivities of such species toward addition and oxida-

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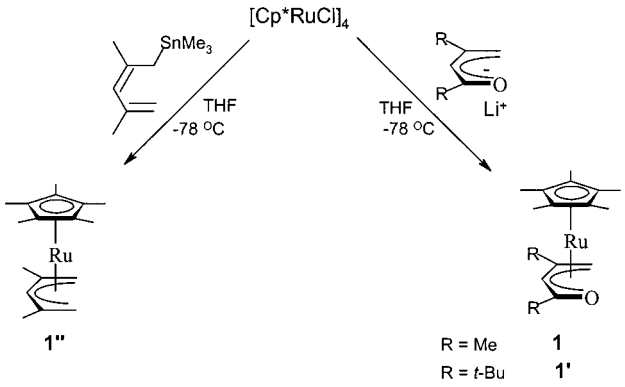
10.1021/om010735s CCC: $22.00
Publication on Web 01/19/2002

tive addition reactions, especially for the mesityl oxide derivative Cp*Ru(η^5-2,4-Me_2-C_4H_3O) (**1**), the bulky Cp*Ru[η^5-2,4-(*t*-Bu)$_2$-C_4H_3O] (**1′**), and the hydrocarbon analogue Cp*Ru(η^5-2,4-Me_2-C_5H_5) (**1″**).

In fact, electrochemical oxidations of compound **1** under argon and oxygen atmospheres have already been described, providing evidence of the formation of Ru(III) as a reactive chemical species,[5] ultimately leading to the Ru(IV) compound Cp*Ru[η^3-$CH_2C(Me)CHC(Me)O$](O_2) (**5**) more efficiently than through the corresponding chemical reaction (70 vs 57%). A number of other d^4 ruthenium(IV) complexes had even earlier been synthesized and studied, particularly regarding their activation of small molecules.[6−14] Recently, increasing attention has been given to the chemistry of precursors containing half-sandwich $[Cp^*Ru(L)_2]^+$ moieties, with L = tertiary phosphines or L_2 = bidentate phosphines[15−17] or diamines.[18] In this regard, intramolecular activation of the pentamethylcyclopentadienyl ligand's C−H bonds has also been observed, for both neutral and cationic Cp*Ru complexes.[19−24] Not uncommonly, methyl ring C−H activations have been found to occur thermally or under the influence of strong bases.[22] However, there is more recent evidence that oxygen-induced methyl C−H activation can occur with surprising facility in Cp*Ru(III) complexes under ambient conditions,[19,23−24] leading to Ru(II) complexes of tetramethylfulvene as products, which exhibit unusual reactivity patterns of their own, as described in detail by Maitlis et al.[19−24] In particular, the stable cationic 16-electron complex $[Cp^*Ru(Me_2NCH_2CH_2NMe_2)]^+$ has been reported to undergo conversion to a Ru(III) complex, and this intermediate eventually activates a methyl C−H bond of the Cp* ligand, giving rise to a hydroxoruthenium tetramethylfulvene complex, [Ru(η^6-$C_5Me_4CH_2$)($Me_2NCH_2CH_2NMe_2$)(OH)]{B[$C_6H_3(CF_3)_2]_4$}.[18]

Scheme 1



In contrast, when chelating diphosphines are used as coligands, reactions with O_2, Cl_2, or H_2 lead to oxidative addition, thereby forming Cp*Ru(IV) complexes, which showed in all cases strong binding between the ruthenium atom and the corresponding activated coordinated molecule.[15−17] An interesting carbon−carbon bond activation was even reported by Moro-oka, which resulted in the 6-methylfulvene complex [Cp*Ru($C_5H_4CHCH_3$)](BF_4) upon stirring Cp*Ru(norbornadiene)Cl[25] in dichloromethane.

In this report, we describe improved synthetic procedures for compounds **1** and **1″**, which involve a reaction between the tetramer $[Cp^*RuCl]_4$ and either the lithium oxopentadienide or the trimethyltinpentadiene reagent, respectively, instead of directly using mesityl oxide or potassium pentadienide, as previously described.[1a] A comparative study of the reactivities of **1**, **1′**, and **1″** has also been undertaken, and the molecular structures of **1**, **1′**, and the functionalized pentamethylcyclopentadienyl complex **6**, the ligand adduct Cp*Ru[η^3-$CH_2C(Me)CHC(Me)O$] (PPh_3) (**7**), and ruthenium(IV) complexes Cp*Ru[η^3-$CH_2C(Me)CHC(Me)O$](Cl)($SnCl_3$) (**2**) and Cp*Ru[η^3-$CH_2C(Me)CHC(Me)O$](O_2) (**5**) are also discussed.

Results and Discussion

The oxopentadienyl compounds **1** and **1′** were formed cleanly at −78 °C from the corresponding lithium oxopentadienides and $[Cp^*RuCl]_4$ in 80 and 88% yields, respectively (Scheme 1). The original synthesis of compound **1** utilized mesityl oxide and presumably entailed a Cp*RuCl(η^4-mesityl oxide) intermediate, which lost HCl in the presence of a mild base in hot THF, giving **1** in ∼65% yield.[1a] The hydrocarbon analogue Cp*Ru(η^5-2,4-C_7H_{11}) (**1″**) has been previously reported,[1a,4b] and we now report an alternate and useful synthetic procedure using $[Cp^*RuCl]_4$ and $C_7H_{11}SnMe_3$ at −78 °C, which led to **1″** in 79% yield (Scheme 1). The constitutions of **1** and **1′** have been confirmed by X-ray structure determinations (Figures 1 and 2, vide infra). A comparative study of the reactivities of compounds **1**, **1′**, and of the hydrocarbon analogue **1″** gave evidence of the

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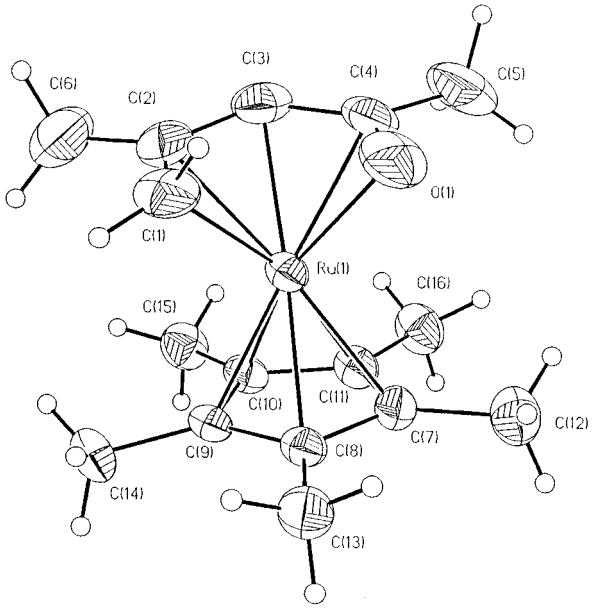

Figure 1. Structure of Cp Ru[η^5-$CH_2C(Me)CHC(Me)O$] (**1**).

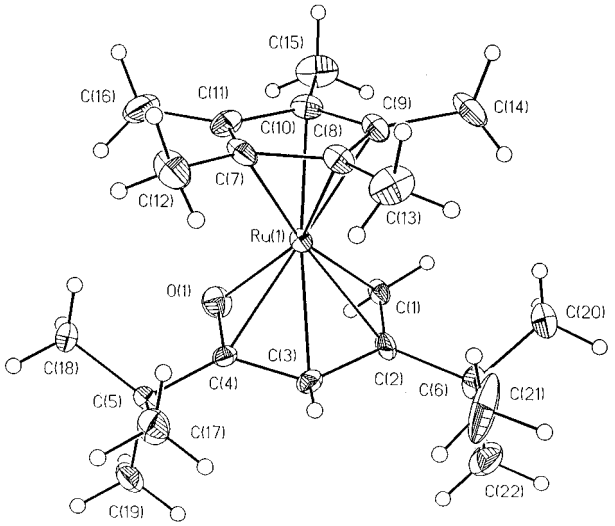

Figure 2. Structure of Cp Ru[η^5-$CH_2C(t\text{-}Bu)CHC(t\text{-}Bu)O$] (**1′**).

higher reactivity of the oxo-derivative **1** toward oxidative additions, as well as in simple ligand addition reactions.

(a) Oxidative Addition Reactions. Oxopentadienyl Compounds. As shown in the oxidative addition reactions described in Scheme 2, new Cp*Ru(IV)(η^3-oxopentadienyl)(X_1)(X_2) compounds **2**−**5** can be synthesized, under very mild conditions, through reactions of Cp*Ru(II)(η^5-2,4-$Me_2C_4H_3O$) (**1**) with $SnCl_4$, I_2, $CHCl_3$, and O_2 respectively. Addition of other potential oxidizing agents, such as CH_3I (1:100) or Me_3SnCl (1:2), to **1** did not lead to reaction even with an excess of reactant and strong refluxing conditions. The ^1H and ^{13}C NMR data of complexes **1**−**5** are summarized in Tables 1 and 2.

The formation of the Sn−Ru bonded compound from the oxidative addition of $SnCl_4$ to **1** at room temperature proceeded in 76% yield. Immediately after addition of the Lewis acid one could observe an orange precipitate of compound **2**, Cp*Ru[η^3-$CH_2C(Me)CHC(Me)O$](Cl)-($SnCl_3$), partially soluble in CH_2Cl_2, $CHCl_3$, and acetone. The structure of **2** was determined through a single-crystal X-ray diffraction study (Figure 3, vide infra).

The iodine and chlorine derivatives were found to exist as mixtures of *endo,anti* and *exo,syn* isomers **3na**, **3xs**, and **4na**, **4xs**, respectively (see Schemes 2 and 3). However, while both chlorine isomers were present at room temperature, for the iodine derivative the reaction initially yielded as a kinetic product the *endo,anti*-oxopentadienyl isomer **3na**, and only at elevated temperatures was there evidence of isomerization to the thermodynamically favored *exo,syn* **3xs** (Scheme 3). After 24 h at 45 °C in $CDCl_3$, these were observed in a 0.05:0.95 ratio according to their respective Cp* signals at 1.96 and 1.95 ppm. After a total of 15 days and 4 months, respectively, three different compounds were easily detected from the corresponding Cp* signals observed at 1.96, 1.95, and 1.69 ppm in 0.54:0.33:0.13 and 0.12:0.36:0.52 ratios, and these were assigned to **3na**, **3xs**, and $[Cp^*RuI_2]_2$.[26] It was also demonstrated that the pure chlorine isomer **4na** underwent partial isomerization, in a sealed NMR tube in $CDCl_3$ after 4 and 15 days at 60 °C, to the **4xs** isomer in 50:50 and 17:83 ratios, accompanied by a small amount of $[Cp^*RuCl_2]_2$ and traces of Cp^*_2Ru. After 56 days, **4na** had been completely consumed, giving evidence of the corresponding kinetic and thermodynamic species. Similar *endo* to *exo* isomerizations have also been described for [CpFe(η^3-$CH_2CR_1CR_2R_3$)(CO)] [R_1 = H, Me; $R_2 = R_3$ = OMe, Cl, H, or OPh],[27] Co(η^3-$CH_2C(Me)CHC(Me)CH_2$)(PMe_3)$_3$,[28] and CpRu(η^3-$CH_2C(Me)CH_2$)(CO).[29] It should be noted that analogous halogen derivatives such as Cp*Ru(η^3-allyl)(X_2) (X = I,[6] Br,[6,7] Cl[7]), Cp*Ru(η^3-oxopentadienyl)$(Br)_2$,[8] and Cp*Ru(η^3-pentadienyl)$(Br)_2$[8] have previously been reported.

Along with isomers **4na** and **4xs**, the reaction between **1** and $CHCl_3$ gave three other compounds. This nonselective reaction produced five fractions after thin-layer chromatography, corresponding to $[Cp^*RuCl_2]_2$ [^1H NMR ($CDCl_3$) $\delta \cong 5.00$ (br)], $(Cp^*)_2Ru$ (δ = 1.84 ppm), **4na**, **4xs**, and a dark green solid, which was not fully characterized.[30] In fact, a number of other activation reactions, in particular when C−C bonds have been involved, have led to the formations of intense green solutions, and various mononuclear,[31] binuclear,[3] or cluster[32a] compounds have been isolated.

Surprisingly, in the presence of traces of air, a THF solution of compound **1**, $BF_3{\cdot}OEt_2$, and *t*-$BuNH_2$ at −78

(26) (a) For Cp^*RuI_2 dimer: ^1H δ = 1.71 (s), ^{13}C δ = 12.98, 99.01 ppm in $CDCl_3$. For Cp^*RuCl_2 dimer: ^1H δ = 5.075−4.85 (broad), ^{13}C δ = not observed. (b) Koelle, U.; Kossakowski, J. *J. Organomet. Chem.* **1989**, *362*, 383.

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(30) The same green powder was formed from reactions of **1**, **1′**, and **1″** with $CHCl_3$. The presence of cationic $[(Cp^*RuCl)_3CH]$ is proposed according to NMR [^1H NMR ($CDCl_3$) δ = 1.69 (Cp*) and 19.9 (CH) ppm; ^{13}C NMR ($CDCl_3$) δ = 11.6 and 97.5 (Cp*) and 342.1 (CH) ppm] and mass spectrum [FAB (glycerol and $CHCl_3$): 828(9), 521(10), 277-(15), 185(100)]. This compound, perhaps accompanied by a Cp^*RuCl_3 counterion, is analogous to a previously reported salts.[32a] Separation of **4na′** from the green soluble product can be carried out chromatographically on alumina by elution with ethanol.

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Scheme 2

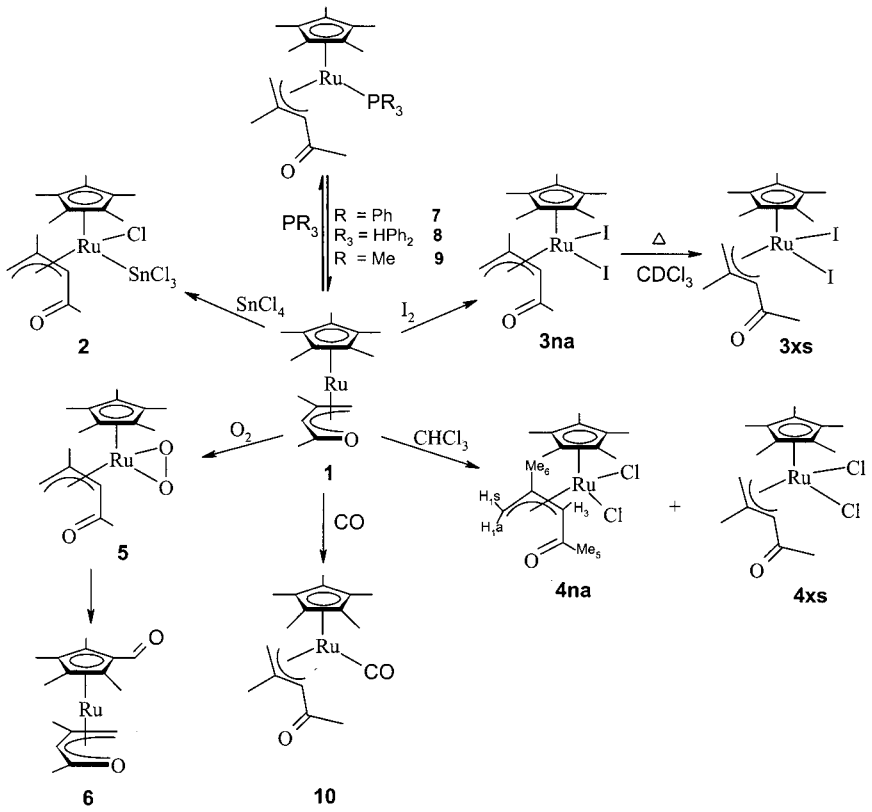


Table 1. ^{1}H NMR Data[a] for Pentadienyl or Oxopentadienyl RuCp* Compounds 1−10

compound	H1 *anti*	H1 *syn*	H3	H(C5)	H(C6)	Cp*
1	2.28	3.25	4.68	1.96	1.48	1.59
	(1.58)[b]	(3.10)	(4.80)	(1.99)	(1.54)	(1.68)
1′	2.12	3.59	5.53	1.14	1.35	1.71
	(1.48)[b]	(3.46) (d, 1.1)	(5.43)	(1.08)	(1.23)	(1.79)
1″[c]	0.36	2.16	4.78	1.73	1.73	1.68
	(−0.02) (d, 2.2)[b]	(1.97) (d, 2.2)	(4.84)	(1.77)	(1.77)	(1.79)
2[b]	3.80	4.40	5.10	2.10	2.30	1.80
2″[b,d]	2.40	3.48	4.08	2.10	2.52	1.75
2a″[b,d]	2.36	3.40	3.90	2.20 (d,1.3)	2.44	1.55
3na	3.78	4.35	5.40	1.59	2.80	1.55
	(3.78)[b]	(4.40)	(5.40)	(2.10)	(2.70)	(1.90)
3xs[b]	1.89	4.16	2.49	2.41	2.77	1.96
3na′[b]	3.98	4.29 (d, 2.0)	5.79 (d, 2.0)	1.48	1.20	1.92
3na″[d]	1.35	2.60	4.25	2.10	2.78	1.40
	(1.85)[e]	(3.00)	(4.16)	(1.95)	(2.50)	(1.78)
4na[b]	3.88	4.10	4.90	2.07	2.44	1.60
4xs[b]	2.17	3.80	2.80	2.40	2.60	1.61
4na′	4.10	4.04 (d, 2.0)	5.52 (d, 2.0)	1.43	1.15	1.52
4na″[b,d]	1.9	3.40	3.90	2.18	2.44	1.55
5	3.40	3.45	4.40	1.62	1.81	1.27
6	2.37	3.34	4.54	1.86	1.31	1.78, 1.73, 1.35, 1.26, 10.29 (CHO)
7[f]	1.00	2.10	1.48	1.99	2.60	1.39
	J_{P-H} = 19.0		J_{P-H} = 15.4			J_{P-H} = 1.3
8[f]	0.97	2.10	1.07	1.68	2.62	1.55
	J_{P-H} = 20.5		J_{P-H} = 15.8			J_{P-H} = 2.6
9[f]	0.78	1.77	1.38	1.88	2.65	1.58
	J_{P-H} = 18.3		J_{P-H} = 15.8			J_{P-H} = 1.5
10	2.60	3.40	3.10	1.54	2.00	1.52

[a] In C_6D_6. δ values are in ppm and J values in hertz. For numbering, see oxopentadienyl ligand in any crystal structure figure or Scheme 2. [b] In $CDCl_3$. [c] References 1a and 4b. [d] Vinylic protons, **2″**: 5.21(s), 5.54 (s); **2a″**: 5.08 (d, J = 2.0), 5.50 (t, J = 2.0); [SnCl*Me*$_2$: 1.25 (J_{SnH} = 8.2), 1.20 (J_{SnH} = 6.7)]; **3na″**: 5.0 (s), 5.27 (s); **4na″**: 5.1 (s), 5.5 (t, J = 1.5). [e] In CD_2Cl_2. [f] Aromatic hydrogens for compounds: **7**, 7.0−7.9 ppm; **8**, 6.9−7.6 ppm; methyl hydrogens for compound **9**, 0.87 ppm (J_{P-H} = 7.4).

°C afforded, after evaporation of THF, the previously reported complex Cp*Ru[η^3-$CH_2C(Me)CHC(Me)O$](O_2) (**5**), in a very low yield (3%), as orange crystals.[33a] The molecular structure of **5** (Figure 4) is described below. In an attempt to avoid polymerization due to the BF_3·OEt_2, and thereby improve the synthesis of **5**, we replaced THF by CH_2Cl_2. However, from a stoichiometric mixture of compounds **1**, BF_3·OEt_2, and *t*-$BuNH_2$, a

Table 2. ^{13}C NMR Data[a] for Pentadienyl or Oxopentadienyl RuCp* Compounds 1−10

compound	C1	C2	C3	C4	C5	C6	CCp*	MeCp*
1	54.8	101.2	84.0	135.0	23.2	25.1	87.1	10.6
1′	48.5 (td, J_{CH} = 150)	117.2	71.7 (dd, J_{CH} = 150)	151.1	31.2 (q, J_{CH} = 126) 35.9	29.4 (q, J_{CH} = 126) 37.8	87.7	11.9 (q, J_{CH} = 126)
1″[b]	45.0 (t, J_{CH} = 154)[c]	92.3	91.5 (d, J_{CH} = 155)	92.3	25.9 (q, J_{CH} = 127)	25.9 (q, J_{CH} = 127)	89.6	10.9 (q, J_{CH} = 124)
2[c]	55.1	117.8	66.8	205.3	34.8	22.8	104.7	9.3
2″[c,d]	64.7	109.4	87.6	142.5	17.4	24.5	102.8	9.5
2a″[c,d]	65.7	108.0	85.7	144.4	18.3	24.7	103.3	9.4
3na	58.5	111.5	63.7	207.2	36.0	26.4	104.0	11.9
3xs[c]	61.3	n.o.	66.8	205.8	33.8	24.2	n.o.	11.8
3na′[c]	50.1	130.6	52.0	216.0	29.7 40.8	26.4 47.4	104.7	12.0
3na″[d]	59.3 (60.2)[e]	104.7 (105.1)	82.4 (83.5)	145.2 (145.0)	24.4 (24.2)	26.3 (26.2)	100.4 (101.6)	11.3 (11.8)
4na[c]	61.8	115.8	70.5	207.3	36.2	20.4	106.8	9.5
4xs[c]	66.7	110.1	70.1	205.7	34.7	18.4	106.5	9.5
4na′[c]	53.9 (t, J_{CH} = 165.3)	132.7	62.4 (d, J_{CH} = 158)	216.0	31.8 (q, J_{CH} = 127) 40.5	26.7 (q, J_{CH} = 127) 47.4	107.5	9.8
4na″[c,d]	65.7	108.0	85.7	144.5	18.4	24.7	103.4	9.4
5	51.8	114.4	61.0	205.6	33.1	18.1	102.7	8.5
6	56.2	103.8	83.0	139.9	23.4	24.5		9.3, 10.4, 190.0 (CHO)
7[d,f]	37.7 J_{P-C} = 6.6	88.1 J_{P-C} = 2.2	47.7 J_{P-C} = 3.3	202.0	34.7	20.1 J_{P-C} = 2.2	89.8	9.6
8[d,f]	37.9 J_{P-C} = 5.4	89.1	51.0	201.7	30.6	19.9	86.5	9.0
9[d,f]	36.0 J_{P-C} = 6.8	83.4	46.7 J_{P-C} = 3.6	200.6	30.8	20.2	88.9	9.8
10[d]	41.0	91.8	58.0	200.5	29.0	24.7	94.3	10.4

[a] In C_6D_6. δ values are given in ppm and J values in hertz. For numbering see oxopentadienyl ligand in the crystal structure figures. [b] References 1a and 4b. [c] In $CDCl_3$. [d] ^{13}C NMR data for compounds: **2″**, 124.2 (−RC=*C*H$_2$); **2a″**, 122.6 (−RC=*C*H$_2$), 12.4, 13.7 (−SnCl*Me*$_2$); **3na″**, 121.5 (−RC=*C*H$_2$); **4na″**, 121.9 (−RC=*C*H$_2$); **7**, 135.3 (d, 8.8 Hz,i), 132.2 (d, 10.8 Hz,o), 129.0 (s,p), 127.1 (d, 10.6 Hz, m); **8**, 135.1 (s, i), 132.7 (d, 9.2 Hz, o), 129.5 (s, p), 128.7 (s, m); **9**, 18.3 ppm (J_{P-C} = 26.5 Hz); **10**, 209.9 ppm. [e] In CD_2Cl_2. [f] ^{31}P NMR data for compound: **7**, 69.9 ppm; **8**, 56.0 ppm, J_{P-H} = 328 Hz; **9**, 7.7 ppm.

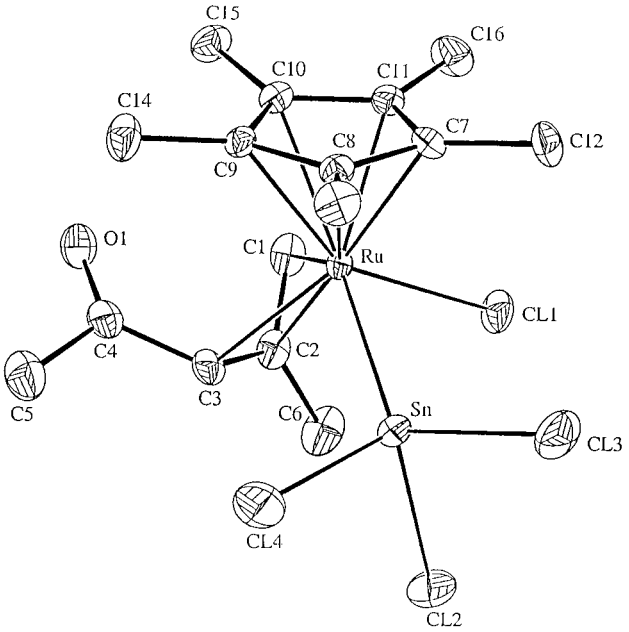
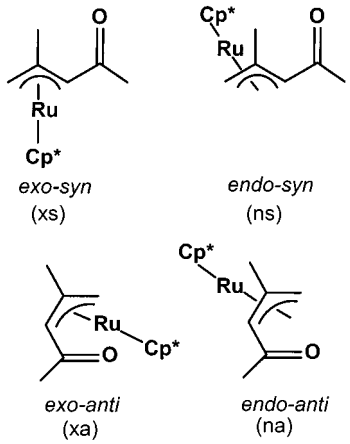


Figure 3. Structure of Cp Ru[η^3-CH$_2$C(Me)CHC(Me)O]-(Cl)(SnCl$_3$) (**2**).

Scheme 3



new product mixture was obtained which again contained complexes **1** and **5**, but also an additional product, **6**, which spectroscopic and crystallographic data revealed to be the previously reported aldehyde derivative [η^5-C$_5$Me$_4$CHO]Ru[η^5-CH$_2$C(Me)CHC(Me)O] (**6**) (Figure 5) resulting from a ring-methyl activation reaction.[5] Ring-methyl activations in pentamethylcyclopentadienyl complexes are not uncommon and, as already mentioned, can be induced by the presence of oxygen, leading to tetramethylfulvene or other types of functionalized polyalkylated cyclopentadienyl complexes (vide supra), such as the aldehyde derivatives [(η^5-C$_5$-Me$_4$CHO)Ru(CO)$_2$X] (X = Cl,Br, I, SCN).[20]

(33) (a) Initial elution of the product mixture on alumina using 1:1 hexane/ether led to a 55% recovery of **1**. Subsequent elution with ether led to two orange bands, the second of which was **5**. (b) We were expecting that compound **1** in the presence of primary *tert*-butylamine would afford, by nucleophilic attack, an azapentadienyl complex, analogous to complex **1**, in a similar manner as the one reported for (oxopentadienyl)Mn(tricarbonyl) complexes.[33c] (c) Cheng, M.-H.; Cheng, C.-Y.; Wang, S.-L.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1990**, *9*, 1853.

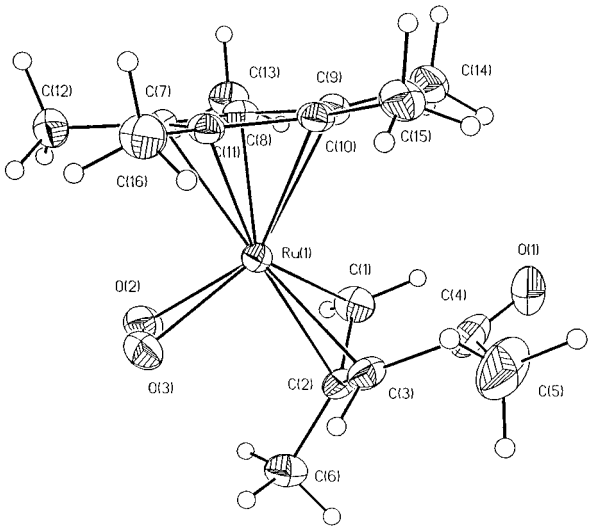


Figure 4. Structure of Cp*Ru[η^3-$CH_2C(Me)CHC(Me)O$]-$(O)_2$ (**5**).

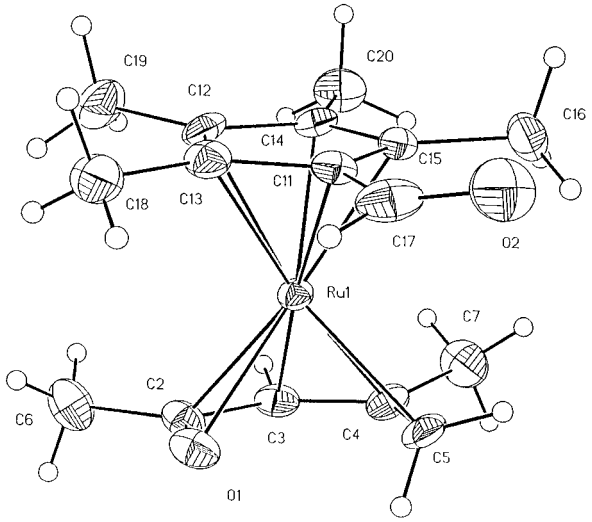


Figure 5. Structure of (η^5-C_5Me_4CHO)Ru[η^5-$CH_2C(Me)$-$CHC(Me)O$] (**6**).

In Scheme 4 a tentative mechanism is proposed for the formation of compound **6**, having compound **5** as an intermediate. The presence of a tetramethylfulvene derivative is in agreement with Maitlis' results for similar ruthenium complexes.[19,22−24] In our case we did not observe a fulvene intermediate, which presumably could lead to immediate regeneration of the aromatic ring functionalized by a hydroperoxide group, and after subsequent loss of water could afford the corresponding aldehyde derivative **6**.

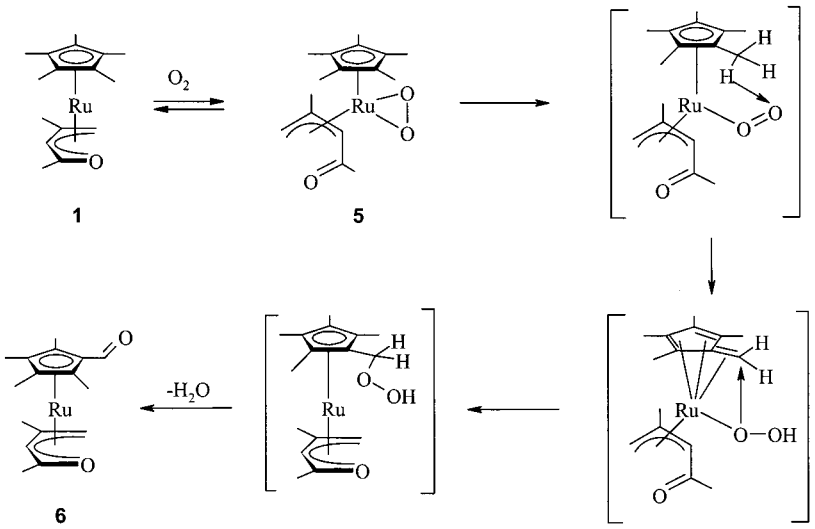
As a result of the apparent ease of $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ interconversions of the oxopentadienyl ligand in compounds **1**, **5**, and **6**, respectively (see Scheme 4), as well as the redox susceptibility of the ruthenium centers [Ru(II) → Ru(IV) → Ru(II)] in each case, we decided to attempt the electrosynthesis of compound **5**. After several modifications of the experimental conditions, we found that electrochemical oxidation of compound **1** under an oxygen atmosphere indeed offered a better synthetic route, providing compound **5** in a yield of 70%. The anodic oxidation of **1** was performed in acetonitrile or nitromethane on a glassy carbon electrode. The electrochemical behavior was found to be strongly dependent on the absence or presence of oxygen in the acetonitrile solutions.[5]

It is important to mention that exposure of compound **1** in CH_3NO_2 to air also gave evidence of formation of **5**, while addition of pure O_2 allowed isolation of complex **5** in 57% yield, even without electrolysis. It was further confirmed that a slow chemical reaction in CH_3CN between $[Cp^*Ru(CH_3CN)_3]PF_6$ and **5** led to the activation of the Cp* ligand in **5** giving compound **6**.[5] Most of the previously reported complexes having an oxygen molecule coordinated to ruthenium atoms have been cationic species, such as $[Cp^*Ru(IV)(\eta^2\text{-}O_2)L_2]^+$ (L_2 = dppe,[15,16] dppm,[16] dippe[17]) in which the O_2 coordination has appeared strong enough to render the complexes relatively unreactive, except when a nitrogen chelate was present ($L_2 = Me_2NCH_2CH_2NMe_2$),[18] giving in that case a tetramethylfulvene complex (vide supra), for which $[Cp^*Ru(IV)(\eta^2\text{-}O_2)L_2]^+$ was tentatively proposed to be an intermediate, although the dioxygen ligand was considered more likely to be a superoxo than a peroxo species.[18]

On the basis of the above, interesting chemistry should be expected from neutral compound **5**. It has already been demonstrated that this complex is remarkably stable at room temperature and that it can also release, under not unduly harsh conditions, the activated oxygen molecule, which could therefore take part in selective oxidation reactions. In fact, passing **5** through a chromatographic column regenerated compound **1**, while activation of the Cp* ligand in compound **5** to give the aldehyde derivative **6** was already evident after heating in C_6D_6 for 20 h at 40 °C. After 10 days at this temperature there was a complete conversion of **5** into **6** and **1** in an approximate 1:0.8 ratio. In an effort to understand this reaction we undertook ^{1}H NMR studies of the interaction of compound **1** with 1 equiv of $BF_3{\cdot}OEt_2$ in C_7D_8. The resulting spectra gave evidence, at low temperature, of the formation of the presumed adduct $Cp^*Ru(OEt_2)(\eta^3\text{-}CH_2C(Me)CH(Me)\text{-}CO{\rightarrow}BF_3)$. At −50, −30, and −10 °C there was no evidence of compound **1**, but new signals at 5.7(s, 1H), 4.2(s, H_{syn}), 3.6(s, H_{anti}) 2.3(s, 3H), 1.6(s, 3H), 1.3(s, 15H), 3.2(q, Et_2O), and 1.2(t, Et_2O) suggested the formation of an η^3-oxopentadienyl complex, due to the coordination to BF_3 by the oxygen atom in compound **1**. Above −10 °C the η^3-oxopentadienyl complex began to eliminate the $BF_3{\cdot}OEt_2$ adduct, and once again the signals from compound **1** began to appear in the ^{1}H NMR spectrum. Finally, at room temperature there were signals for compound **1** (1.92, 4.6, 1.45, 3.18, 2.1, 1.58, see Table 1), along with the corresponding signals for $Cp^*Ru(OEt_2)(\eta^3\text{-}CH_2C(Me)CH(Me)CO{\rightarrow}BF_3)$ in a 1:0.9 ratio.

In the case of the oxopentadienyl compound **1′**, with bulky *tert*-butyl groups present on C2 and C4, the corresponding oxidative addition reactions proceeded much more slowly than those with just methyl group substituents, such as **1** and **1″**. The reaction of **1′** with I_2 and $CHCl_3$ led to the isolable compounds **3na′** and **4na′** (analogous to **3na** and **4na** in Scheme 2) in 63% and 25% yields, respectively. The ^{1}H and ^{13}C NMR data for **3na′** and **4na′** are listed in Tables 1 and 2. As had been observed for compounds **3** and **4**, compounds **3na′** and **4na′**, in $CDCl_3$ solution, were found to occur as inseparable mixtures with the corresponding $[Cp^*RuX_2]_2$

Scheme 4



molecules [X = Cl, ^{1}H NMR ($CDCl_3$) $\delta \approx 5.0$ (br) (vide infra), X = I, ^{1}H NMR ($CDCl_3$) δ 1.71 (s), ^{13}C NMR δ 13.1, 96.0],[26] while there was also evidence of the free α,β-unsaturated ketone [*t*-BuC(O)CHC(Me)*t*-Bu]. As was the case for **1** and $CHCl_3$, the reaction of **1′** with $CHCl_3$ was found through ^{1}H NMR to lead to a complex mixture of **4na′** and $[Cp^*RuCl_2]_2$, along with other species that were not characterized, but displayed a sharp singlet at 1.69 ppm[30] and a broad singlet at 1.78 ppm.

Monitoring the reaction of **1′** and Me_2SnCl_2 in benzene or THF showed that there was no oxidative addition; instead, and after only 2 days, there was evidence of free α,β-unsaturated ketone [*t*-BuC(O)CHC(Me)*t*-Bu], along with starting materials. After 70 h at 40−45 °C, there was a 1:0.85 ratio of free ketone and **1′**, respectively. In contrast, **1′** and $SnCl_4$ gave a bright orange solution at −78 °C, but as soon as the temperature increased, the product became dark brown, and several attempts to isolate the orange product at low temperature failed. Although not all of these reactions led to isolable products, it may in any case be recognized that the presence of bulky *tert*-butyl substituents considerably reduced the reactivity of the oxopentadienyl compound **1′** compared to **1**.

Pentadienyl Compounds. Analogous pentadienyl compounds **2″**, **3na″**, **4na″**, and $Cp^*Ru[\eta^3\text{-}CH_2C(Me)CHC(Me)CH_2](Cl)(SnMe_2Cl)$ (**2a″**) were formed by the oxidative additions of $SnCl_4$, I_2, $CHCl_3$, and Me_2SnCl_2 with $Cp^*Ru[\eta^5\text{-}CH_2C(Me)CHC(Me)CH_2]$ (**1″**). Comparatively, **1″** reacted more slowly than the corresponding oxopentadienyl compound **1**. The previously described oxodienyl products **2**, **3na**, **3xs**, **4na**, and **4xs** were relatively easily isolated compared to their corresponding pentadienyl complexes. Of these, only **3na″** could be isolated and fully characterized, while the formulations of other species have had to rely on spectroscopic data (see Tables 1 and 2). Also, it was observed that attempts, even in chloroform, to recrystallize samples of **2″** afforded every time less soluble species, which suggested that reactive species are involved and that they undergo transformation during the purification process. Seven milligrams of compound **2a″** was isolated, and this sample was found to convert in chloroform solution to the corresponding compound **4na″**, suggesting a labile Ru−Sn bond. The small quantity and low stability of **2a″** prevented its characterization by elemental analysis. No reaction was observed for the less acidic Me_3SnCl.

Stirring compound **1″** in $CHCl_3$ at room temperature afforded **4na″**, along with the paramagnetic $[Cp^*RuCl_2]_2$, and a deep green solid,[30] which was recrystallized from $CHCl_3/Et_2O$, yielding a mostly green powder, in which a few red crystals were observed. The red crystals corresponded to a novel and interesting C−C coupling product in which the pentadienyl ligand was converted to an η^6-toluene molecule coordinated to the Cp*Ru fragment. This cationic complex is accompanied by a paramagnetic Cp^*RuCl_3 counterion. The formation of $[Cp^*Ru(\eta^6\text{-}C_7H_8)][Cp^*RuCl_3]$ (**11**) (Figure 6, vide infra) along with the Cp^*RuCl_2 dimer in the same reaction suggested an equilibrium between the dimer and chloride ions, forming the anionic fragment, which is favored in the presence of the large and very stable cation $[Cp^*Ru(\eta^6\text{-}C_7H_8)^+]$. A high affinity for aromatic hydrocarbons has been previously reported for the Cp^*Ru^+ fragment,[8,34,35] and aromatization of hydrocarbons by the electrophilic "Cp^*Ru^+" fragment has also been observed.[32,34] The mechanism for the cyclization of the 2,4-dimethylpentadienyl fragment through C−C activation is unclear. Recently, Salzer[36] et al. reported the isolation of $[Cp^*Ru(toluene)]^+$ from attempts to prepare Cp*Ru(2,4-dimethylpentadienyl) complexes in EtOH. While they proposed that formation of this cationic complex was due to the presence of traces of toluene in the EtOH, it is also possible, if not more likely, that the toluene ring was formed in situ, as in the case of compound **11**, which was prepared in chloroform.

The higher yields for the isolation of the Ru(IV) derivative $Cp^*Ru[\eta^3\text{-}CH_2C(R_1)CHC(R_1)R_2](Cl)(X)$ [R_1 = Me, R_2 = O, X = $SnCl_3$], **2**, as compared to the R_1 = Me, R_2 = CH_2; X = $SnCl_3$, **2″**, or $SnMe_2Cl$, **2a″**, analogues, and the lack of formation of the corresponding derivative for R_1 = *t*-Bu, R_2 = O, and X = $SnCl_3$, may be attributed

(34) (a) Carreno, R.; Urbanos, F.; Dahan, F.; Chaudret, B. *New J. Chem.* **1994**, 18, 449. (b) Masuda, K.; Ohkita, H.; Kurumatani, S.; Itoh, K. *Organometallics* **1993**, *12*, 2221.

(35) (a) Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981. (b) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.

(36) Bauer, A.; Englert, U.; Geyser, S.; Podewils, F.; Salzer A. *Organometallics* **2000**, *19*, 5471.

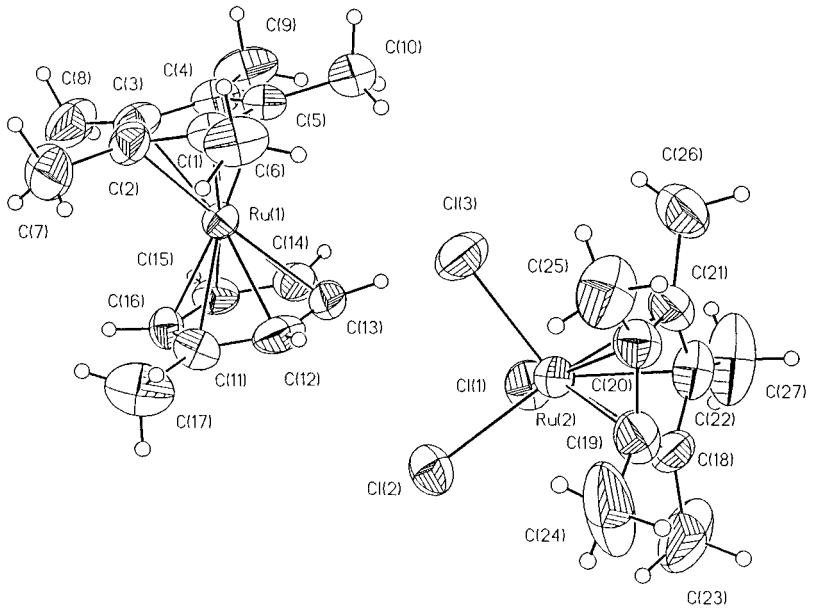


Figure 6. Structure of [Cp*Ru(η^6-C_7H_8)][Cp*$RuCl_3$] (**11**).

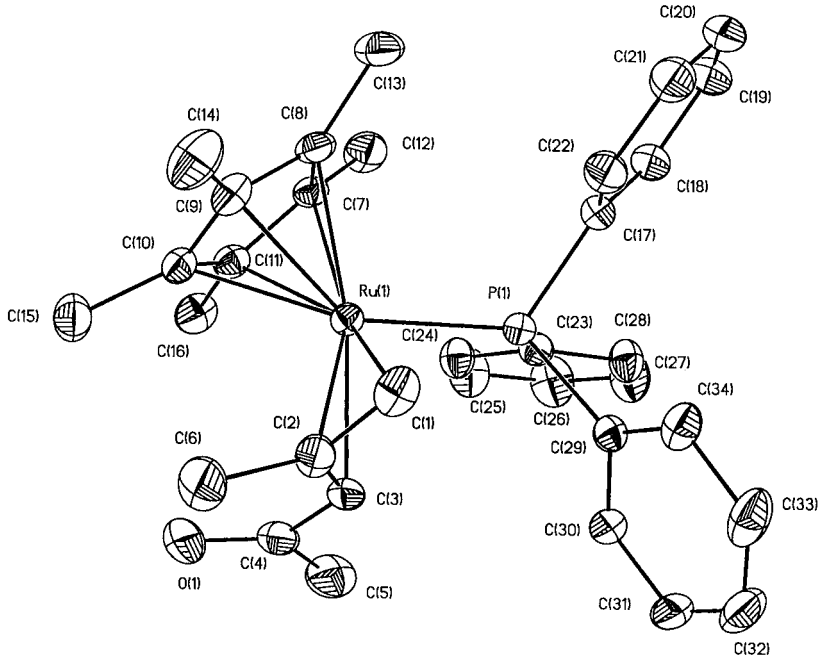


Figure 7. Structure of Cp*Ru[η^3-CH_2C(Me)CHC(Me)O]PPh_3 (**7**).

to the higher reactivity of the Cp*Ru(η^5-2,4-dimethyloxopentadienyl) complex. This fact can be explained by an increase in facility of the $\eta^5 \leftrightarrow \eta^3$ interconversion for the harder, more electronegative oxopentadienyl ligand. The lack of formation of the corresponding derivatives for R_1 = *t*-Bu, R_2 = O, and X = $SnCl_3$ may be traced to the increased steric effects of the *tert*-butyl substituents.

(b) Addition Reactions. Oxopentadienyl Compounds. The addition of phosphines, PR_3 (R = Ph, Me or R_3 = HPh_2), in cyclohexane to compound **1** led to the formation of compounds **7**−**9** as described in Scheme 2. The complexes are air-stable in the solid state but readily oxidized in solution. The addition reactions generally proceed much more slowly than the oxidative additions. For example, 1 equiv of triphenylphosphine in a cyclohexane solution of compound **1** was heated under reflux for 7.5 h, but after workup (see Experimental Section), only a 13% yield of Cp*Ru[η^3-CH_2C(Me)CHC(Me)O]PPh_3 (**7**) was obtained (Figure 7). Even with prolonged reaction times (22 h), excesses of PPh_3 (2:1), or a change in solvent (THF), the yields were not improved, and in each case, significant quantities of compound **1** remained, necessitating an inconvenient separation of **1** and **7**, whether through recrystallization or sublimation, even after chromatography. Through ^1H and ^{31}P NMR studies of pure compound **7** in C_6D_6 the facile dissociation of PPh_3 became evident, along with the consequent formation of compound **1**. After 24 h at 45 °C one could clearly observe from ^{31}P NMR the presence of free phosphine, compound **7**, and a new compound with a signal at δ = 41 ppm, which was not characterized. ^1H NMR demonstrated that compounds **1** and **7** were present in an 8:2 ratio, which changed to

Table 3. Crystal Data for 1, 1′, 2, 5, 6, 7, and 11

	$C_{16}H_{24}ORu$ (**1**)	$C_{22}H_{36}ORu$ (**1′**)	$C_{16}H_{24}OCl_4SnRu$ (**2**)	$C_{16}H_{24}O_3Ru$ (**5**)	$C_{16}H_{22}O_2Ru$ (**6**)	$C_{34}H_{39}OPRu$ (**7**)	$C_{27}H_{38}Cl_3Ru_2$ (**11**)
mol wt	333.42	417.58	593.941	365.42	347.41	595.69	671.06
cryst syst	$P2_12_12_1$	$P2_12_12_1$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	10.485(2)	11.604(2)	8.829(2)	8.829(2)	9.841(3)	18.380(2)	8.4583(10)
b (Å)	11.720(2)	13.304(3)	15.605(3)	8.526(2)	13.594(4)	9.6947(7)	26.5482(10)
c (Å)	12.401(2)	13.488(3)	15.274(3)	21.244(4)	11.172(12)	18.467(2)	12.5414(10)
α (deg)	90.00	90.00	90.00	90.00	90.000(12)	90.000(2)	90.0000(10)
β (deg)	90.00	90.00	96.64(2)	99.98(3)	92.89(6)	117.628(10)	90.781(10)
γ (deg)	90.00	90.00	90.00	90.00	90.00(6)	90.000(10)	90.000(10)
V (Å^3)	1523.9(5)	2082.3(8)	2090.31	1575.0(6)	1492.7(17)	2915.4(5)	2815.9(4)
Z	4	4	4	4	4	4	4
cryst size (mm)	0.31 × 0.3 × 0.28	0.22 × 0.22 × 0.11	0.31 × 0.28 × 0.25	0.4 × 0.4 × 0.3	0.5 × 0.4 × 0.23	0.4 × 0.3 × 0.2	0.17 × 0.17 × 0.11
abs coeff (mm^{-1})	1.016	0.758	2.4271	1.000	1.046	0.617	1.371
D_{calcd} (g cm^{-3})	1.453	1.332	1.887	1.541	1.546	1.357	1.583
scan type	$\omega/2\theta$	$\omega/2\theta$	$\theta/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
total no. of data	2704	2142	4088	2852	1472	6956	5547
total no. of unique data	1345	2082	3670	2770	1400	6361	4921
total no. of obsd data, $F>4\sigma(F)$	1154	1769	3109[a]	1971	1400	4361	2454
final R1	0.0326	0.0412	0.0205	0.0330	0.0367	0.0329	0.0461
final wR2	0.0766	0.1120	0.0356	0.0835	0.0951	0.0895	0.1261
no. of variables	164	218	209	181	172	340	289

[a] $(F_o)^2 > 3\sigma(F_o)^2$.

9:1 after 15 days, but thereafter remained constant for at least 3 months.

A stoichiometric reaction between compound **1** and PPh_3 in THF, under UV irradiation with a medium-pressure lamp, was carried out for 4.5 h, producing four signals in the ^{31}P NMR spectrum at 67.2, 56.3, 39.4, 26.6 ppm in a 0.57:0.65:1.0:0.58 ratio, respectively. Purification by chromatography afforded only one phosphine complex, accompanied by compound **1**; the former compound was characterized as the $PHPh_2$ complex **8** (Scheme 2; $\delta = 56.3$ ppm, $J_{P-H} = 329$ Hz), formed via a P−C bond cleavage reaction.

The stoichiometric photochemical reaction of **1** with the $PHPh_2$ ligand in THF solution was found to be less selective than the corresponding reaction with PPh_3. After 4.5 h of irradiation and removal of solvent in a vacuum, the reaction mixture gave a brown solid and an oily fraction after washing with hexane. The brown solid appeared, by ^{31}P NMR, to be composed of at least six different species ($\delta = 66.3$, 53.8, 36.5, 31.5, 21.4, and −5.7 ppm). Additionally, a broad band was observed between 47.9 and 21.4 ppm, while the oily fraction showed three signals at 64.9, 53.9, and −15.8 ppm. After chromatography on silica gel with ether as the eluant, there were two signals at 66.7 and 56.0 ppm. Sublimation under reduced pressure at 70 °C partially removed compound **1**, and the remaining product, which did not sublime, was compound **8** (^{31}P $\delta = 55.5$ ppm, $J_{P-H} = 328$ Hz) contaminated with **1**.

A stoichiometric reaction between compound **1** and PMe_3 under reflux for 6 h in cyclohexane yielded an orange product, which could be isolated after chromatography and sublimation or recrystallization (see Experimental Section), although it appeared to have limited stability in solution. The product Cp*Ru[η^3-$CH_2C(Me)CHC(Me)O$]PMe_3 (**9**) was obtained in the highest (70%) yield of all the phosphine adducts, likely due to the basicity and small size of PMe_3. The ^1H, ^{13}C, and ^{31}P NMR data for compounds **7**−**9** are reported in Tables 1 and 2, and the crystal structure of **7** (Figure 7) is described below. Phosphine derivatives **7**−**9** were observed exclusively as the *exo-syn* derivatives, probably due to the harsh experimental conditions required to obtain the addition products. Similar attempts with triphenyl phosphite did not lead to clean reactions.

The addition of CO, at atmospheric pressure, to a solution of compound **1** in refluxing THF gave after 10 h evidence by IR of decoordination by the CO of the oxopentadienyl ligand (1668 cm^{-1}, THF). An IR spectrum of a hexane solution of unreacted **1** and product **10** (Cp*Ru[η^3-$CH_2C(Me)CHC(Me)O$]CO) revealed the presence of a carbonyl ligand in **10** (1962 cm^{-1}, hexane). The similar solubilities of compounds **1** and **10** did not allow for the separation of these two compounds, which, by ^1H NMR, were present in an approximate ratio of 0.56:0.44. The ^1H and ^{13}C NMR data for compound **10** are reported in Tables 1 and 2. Similar compounds, such as CpRu(η^3-CH_2CRCH_2)(CO) (R = H, Me), have been reported to arise from the phase transfer reaction of allyl bromides or chlorides with $CpRu(CO)_2X$ (X = Cl, Br).[29] The chloride derivative gave a mixture of *endo* and *exo* isomers in a 1:1 ratio, while the addition of CO to compound **1** under THF reflux gave only the *exo-syn* isomer.

Neither the oxopentadienyl compound **1′** nor the hydrocarbon analogue **1″** underwent addition reactions even after at least 13 h with PPh_3 under THF reflux, PMe_3 or CO.

Structural Studies. Crystal data for compounds **1**, **1′**, **2**, **5**, **6**, **7**, and **11** are provided in Table 3. The structures of **1** and **1′** are presented in Figures 1 and 2. These are generally similar to those of related species.[1a] Some relevant data are provided in Table 4. The solid state structures of the oxidative addition products **2**, **5**, and **11** and the PPh_3-coordinated complex **7** are presented in Figures 3, 4, 6, and 7, respectively, while various bonding parameters are contained in Tables 5 and 6. The solid state structure of compound **6** is

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compounds 1, 1′, and 6

	1	1′	6
	Bond Lengths		
Ru−C1	2.160(8)	2.142(7)	2.176(7)
Ru−C2	2.161(10)	2.210(8)	2.178(7)
Ru−C3	2.180(8)	2.227(7)	2.188(7)
Ru−C4	2.170(7)	2.223(7)	2.196(7)
Ru−C7	2.170(8)	2.237(8)	2.219(7)
Ru−C8	2.158(7)	2.192(7)	2.182(7)
Ru−C9	2.143(6)	2.155(7)	2.151(7)
Ru−C10	2.172(7)	2.148(8)	2.141(8)
Ru−C11	2.204(8)	2.176(8)	2.183(7)
Ru−O1	2.167(5)	2.161(6)	2.152(5)
O1−C4	1.348(11)	1.333(9)	1.294(8)
O2−C17			1.184(10)
C1−C2	1.346(15)	1.344(12)	1.383(10)
C2−C3	1.424(14)	1.436(10)	1.413(10)
C3−C4	1.398(13)	1.439(10)	1.425(10)
C4−C5	1.494(15)	1.516(10)	1.491(10)
C2−C6	1.500(17)	1.525(12)	1.500(11)
C−C (Cp*)	1.423(5)	1.423(5)	1.427(4)
C−Me (Cp*)	1.497(5)	1.500(5)	1.499(4)
	Bond Angles		
C1−C2−C3	121.0(12)	119.8(7)	121.3(7)
C1−C2−C6	120.5(13)	120.3(8)	121.4(7)
C2−C3−C4	126.0(11)	124.6(7)	125.2(7)
C3−C2−C6	117.1(7)	119.5(8)	117.1(7)
C3−C4−C5	121.2(7)	119.3(7)	121.2(7)

presented in Figure 5, and bonding parameters are given in Table 4.

The bonding for the oxodienyl ligands in **1** and **6** appears similar, with respective average values for the Ru−C(1−4) and Ru−O bonds being 2.168(6), 2.170(6), 2.184(6), 2.183(5), and 2.160(4) Å. The corresponding distances for **1′** (Table 4) reflect a significant steric effect of the *tert*-butyl substituents, as the values for the internal ligand atoms (C2−4) are lengthened, while the values for the C1 and O1 do not experience significant lengthening. It appears that the steric interaction also has affected the bonding for the cyclic ligand as well, as the average Ru−C(Cp*) distance for **1′** is 2.182 Å, vs an average of 2.172 Å for **1** and **6**. One further point of interest relates to the potential for disorder for the open oxodienyl ligands. The fact that identical substituents are present on the carbon atoms in the 2 and 4 positions might be expected to favor such a possibility, although the well-behaved refinements and general lack of mirror plane symmetry in bonding parameters for the open ligands indicate that any disorder is minor. Nonetheless, the O1−C4 distance in **6** is at least slightly shorter than those in **1** and **1′**, and it is possible that the presence of a polar substituent on the cyclic dienyl ligand in **6** could have played a role in reducing the extent of disorder, whether through inter- or intramolecular interactions. The CHO group in the cyclic ligand of complex **6** displays a typical C═O bond length of 1.184(10) Å, along with significant shortening for the C−CHO bond [1.456(10) Å] compared to 1.504(9) Å for the C−CH_3 bonds in the Cp* fragment of compound **1**.

The structural parameters for **2**, **5**, and **7** correspond in general fairly closely to each other, despite the fact that the first two are Ru(IV) complexes, while the last is Ru(II). In fact, the Ru−C bond distances in **2** are those which stick out, being generally longer than those of **5** or **7** (e.g., Ru−C(Cp*) = 2.258, 2.233, and 2.234 Å, respectively). This may reflect a greater steric problem in accommodating extra $SnCl_3$ and Cl ligands, as opposed to either a single O_2 or PPh_3 ligand. Each complex contains an η^3-oxodienyl ligand, coordination preferentially being observed through carbon atoms (I) rather than through an oxoallyl (II) (Scheme 5). Such is to be expected based on the soft nature of Ru(II) and is consistent with observations made for related η^3-oxodienyl and η^4-dienal ligands.[37] The bonding parameters within the ligands are quite similar, with an average delocalized C−C distance of 1.410(4) Å, and an average C═O distance of 1.215(5) Å, similar to the value of 1.184(10) Å for the aldehyde substituent in **6** (vide supra).

The Ru−Sn and Ru−Cl bond distances in compound **2**, 2.6002(4) and 2.4002(9) Å, are longer and shorter, respectively, than those in Ru(II) compounds such as Cp*$RuSnCl_3$(COD)[38] [2.5855(4) Å] and CpRuX(Ph_2PCH(Me)CH_2PPh_2] [X = Cl,[39] 2.444(2) Å; X = $SnCl_3$,[39] 2.551(1) Å], or LRuCl(PHPh_2)(PPh_3) [L = Cp 2.434(2); L = Cp* 2.462(2) Å].[40] Similar Ru−Cl distances have been observed for Ru(IV) compounds such as [Cp*$RuCl_2$($Ph_2PCH_2CH_2PPh_2$)]CF_3SO_3[41] [2.397(1) and 2.390(1) Å] and CpRuCl_2(η^3-C_4H_4OMe)[42] [2.403(1) Å].

In compound **5** the dioxygen is symmetrically bound to ruthenium (Ru−O ∼1.993(3) Å) with an O2−O3 distance of 1.416(5) Å, which is much longer than that in the superoxide KO_2 (1.28 Å),[43a] but slightly shorter than that in H_2O_2 (1.46 Å).[43b] The O−O and two Ru−O distances are longer and shorter, respectively, compared to those observed for many cationic dioxygen complexes such as [Cp*Ru(O_2)L_2][X] {L_2 = $Ph_2PCH_2CH_2PPh_2$, X = BPh_4[16] [1.37(1), 2.003(9), and 2.002(9) Å], X = PF_6[15] [1.398(5), 2.040(3), and 2.023(3) Å], X = BPh_4[17] [1.37(1), 2.028(9), and 2.021(9) Å], L_2 = Ph_2PCpFeCpPPh_2 (dppf), X = BF_4[44] [1.381(11), 2.036(8), and 2.029(8) Å], and [RuH(O_2)(dippe)$_2$][BPh_4][45,46] [1.36(1), 2.04(1), and 2.00(1) Å]. A similar O−O bond length has been observed, however, for [Rh(O_2)(dppe)$_2$][PF_6] (1.418(11) Å).[47]

The crystal structure of compound **11** confirms the susceptibility of the electrophilic fragment "Cp*Ru^+" to coordination by aromatic ligands,[34,35] as well as by chlorine atoms. The compound consists of two fragments: the cationic [Cp*Ru(η^6-toluene)]$^+$ sandwich and the anionic half-sandwich [Cp*$RuCl_3$]$^-$, both with crystallographic mirror symmetry. The structure of the anionic fragment corresponds to a piano stool geometry.

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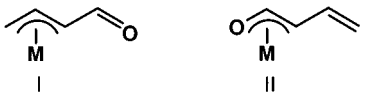
Table 5. Selected Bond Lengths (Å) and Angles (deg) for Compounds 2, 5, and 7

compound **2**		compound **5**		compound **7**	
		Bond Lengths			
Sn−Ru	2.6002(4)	Ru−O2	1.994(3)	Ru−P1	2.3205(8)
Sn−Cl2	2.359(1)	Ru−O3	1.991(3)	P1−C17	1.842(3)
Sn−Cl3	2.360(1)	O2−O3	1.416(5)	P1−C23	1.836(3)
Sn−Cl4	2.380(1)			P1−C29	1.857(3)
Ru−Cl1	2.4002(9)				
Ru−C1	2.218(4)		2.156(5)		2.189(3)
Ru−C2	2.216(4)		2.150(4)		2.145(3)
Ru−C3	2.266(4)		2.199(4)		2.223(3)
Ru−C7	2.233(3)		2.182(4)		2.254(3)
Ru−C8	2.282(3)		2.172(4)		2.226(3)
Ru−C9	2.296(3)		2.252(4)		2.211(3)
Ru−C10	2.278(3)		2.313(4)		2.243(3)
Ru−C11	2.203(3)		2.253(4)		2.251(3)
O1−C4	1.214(5)		1.211(7)		1.220(4)
C1−C2	1.400(6)		1.414(6)		1.407(5)
C2−C3	1.411(6)		1.423(6)		1.431(5)
C3−C4	1.489(6)		1.479(8)		1.460(5)
C4−C5	1.512(6)		1.514(8)		1.504(6)
C2−C6	1.505(6)		1.494(7)		1.509(5)
C−C (Cp*)	1.431(3)		1.425(3)		1.422(2)
C−Me (Cp*)	1.490(3)		1.496(3)		1.507(2)
		Bond Angles			
Ru−Sn−Cl2	122.83(4)	O3−Ru−O2	41.64(14)	Ru−P1−C17	113.76(10)
Ru−Sn−Cl3	121.22(3)	Ru−O3−O2	69.3(2)	Ru−P1−C23	117.40(10)
Ru−Sn−Cl4	116.13(3)	Ru−O2−O3	69.1(2)	Ru−P1−C29	120.05(10)
C1−C2−C3	118.0(4)	C1−C2−C3	116.9(4)	C1−C2−C3	115.8(3)
C2−C3−C4	125.0(4)	C2−C3−C4	124.9(5)	C2−C3−C4	126.5(3)
C3−C4−C5	115.5(4)	C3−C4−C5	113.0(6)	C3−C4−C5	115.3(3)
C1−C2−C6	121.5(4)	C1−C2−C6	122.1(4)	C1−C2−C6	120.2(3)
C3−C2−C6	120.4(4)	C3−C2−C6	120.6(4)	C3−C2−C6	123.9(4)
O1−C4−C3	124.4(4)	O1−C4−C3	124.6(5)	O1−C4−C3	126.1(4)
O1−C4−C5	119.9(4)	O1−C4−C5	122.2(6)	O1−C4−C5	118.4(4)
Cl2−Sn−Cl3	95.61(5)			C17−P1−C23	104.46(15)
Cl2−Sn−Cl4	97.14(5)			C17−P1−C29	100.53(13)
Cl3−Sn−Cl4	98.57(5)				
Sn−Ru−Cl1	77.45(3)				

Table 6. Selected Bond Lengths (Å) and Angles (deg) for Compound 11

Ru1−C1	2.147(8)	C1−C2	1.395(17)	C1−Ru1−C2	38.1(3)
Ru1−C2	2.178(7)	C1−C5	1.422(12)	C1−Ru1−C3	64.4(3)
Ru1−C3	2.167(7)	C1−C6	1.510(11)	C4−Ru1−C5	39.0(3)
Ru1−C4	2.149(8)	C2−C3	1.438(13)	C3−Ru1−C5	64.2(3)
Ru1−C5	2.167(7)	C3−C4	1.379(12)	C1−Ru1−C11	116.6(3)
Ru1−C11	2.208(8)	C4−C5	1.439(11)	C2−Ru1−C11	108.9(3)
Ru1−C12	2.215(8)	C11−C12	1.375(13)	C4−Ru1−C11	167.4(3)
Ru1−C13	2.219(8)	C11−C16	1.385(11)	C5−Ru1−C14	115.7(3)
Ru1−C14	2.210(8)	C11−C17	1.487(14)	Cl1−Ru2−Cl2	89.45(9)
Ru1−C15	2.213(8)	C12−C13	1.380(15)	Cl1−Ru2−Cl3	94.11(10)
Ru1−C16	2.182(7)	C13−C14	1.393(15)	Cl3−Ru2−Cl2	89.35(10)
Ru2−Cl1	2.405(3)	C14−C15	1.411(13)	Cl1−Ru2−C21	116.3(3)
Ru2−Cl2	2.410(2)	C15−C16	1.402(12)	Cl1−Ru2−C18	104.0(3)
Ru2−Cl3	2.381(2)	C18−C19	1.468(15)	Cl1−Ru2−C22	92.6(2)
Ru2−C18	2.149(7)	C18−C22	1.420(14)	Cl2−Ru2−C22	145.9(3)
Ru2−C19	2.194(9)	C18−C23	1.474(12)	Cl3−Ru2−C18	154.5(2)
Ru2−C20	2.187(8)	C19−C20	1.402(13)	Cl3−Ru2−C19	123.7(4)
Ru2−C21	2.163(8)	C20−C21	1.394(13)	Cl3−Ru2−C22	124.4(3)
Ru2−C22	2.169(9)	C21−C22	1.363(12)	Ru1−C11−C17	129.6(7)

Scheme 5



I II

As expected, the Ru−C distances for the arene ligand are somewhat longer than those for the C_5Me_5 ligands in either the cationic or anionic portions, the respective averages being 2.208(3) vs 2.162(4) and 2.172(5) Å. The Ru−Cl distances [2.405(3), 2.410(2), and 2.381(2) Å] have typical values for Ru(IV) compounds.[41,42] A similar but not isomorphous compound, [Cp*Ru(η^6-C_6H_6)]-[Cp*$RuBr_3$], has been previously reported.[8]

Summary

As a result of these studies, it is apparent that the reactivities of the half-open ruthenocenes and their oxodienyl analogues are strongly influenced by steric and electronic properties of both the metal complex and the incoming reactant, whether simple coordination or oxidative addition is involved. Perhaps the clearest observation to be made from this work is that while the oxodienyl complexes undergo reactions similar to their all-carbon analogues, the oxodienyl species generally appear more reactive, a feature that can be traced to the expected weaker coordination by the hard oxygen center as compared to the softer carbon centers. A par-

ticularly interesting illustration of this is the formation of the neutral aldehyde derivative **6** from **5**, a transformation not observed to date for the more common, cationic O_2 complexes. Interestingly, azadienyl complexes have been found to display behavior sometimes similar to that of their isoelectronic pentadienyl and oxodienyl complexes, but at other times different. Further studies to gain a better understanding of the relationships between these types of compounds are continuing.

Experimental Section

Standard inert-atmosphere techniques were used for all syntheses and sample manipulations. The solvents were dried by standard methods (hexane and pentane with CaH_2, diethyl ether and THF with Na/benzophenone, CH_2Cl_2 and $CHCl_3$ with $CaCl_2$, benzene and toluene with Na, CH_3CN with P_2O_5) and distilled under argon prior to use. Compounds $[Cp^*RuCl]_4$,[35b] $[Cp^*Ru(CH_3CN)_3]^+$,[35b,48] **5**,[5] and 2,2,5,6,6-pentamethyl-4-hepten-3-one[49] were prepared according to literature procedures. Iodine was resublimed and mesityl oxide distilled under reduced pressure. All other chemicals were used as purchased from Sigma-Aldrich, Strem Chemicals, Merck, and J. T. Baker. Elemental analyses were performed by Robertson Microlit Laboratories, Inc., Madison, NJ, and E&R Microanalytical Labs. Solution IR spectra were recorded on a Perkin-Elmer 6FPC-FT spectrophotometer using a $CHCl_3$ or CCl_4 solution cell with NaCl plates. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on JEOL 90 MHz, JEOL GSX-270, JEOL Eclipse-400 MHz, or Bruker 300 MHz spectrometers in deoxygenated, deuterated solvents. NMR chemical shifts are reported relative to TMS and ^{31}P NMR chemical shifts relative to 85% H_3PO_4. Mass spectra were obtained with a Hewlett-Packard HP-5990A, Finnigan MAT95 (FAB), or Finnigan LCQ ion trap instrument. Ionization was by electrospray from a solution of MeOH/H_2O/acetic acid, 50:49:1 vol %, or a Micromass ZAB-SE magnetic sector instrument. Ionization was by FAB with xenon atoms at 6 keV energy (Washington University, St. Louis, MO); *m*/*z* values are given relative to ^{102}Ru, ^{35}Cl, and ^{119}Sn isotopes. Melting points were determined using a Mel-Temp apparatus and are not corrected.

Synthesis of Cp*Ru[η^5-$CH_2C(Me)CHC(Me)O$] (1). Under a nitrogen atmosphere, a *n*-BuLi (1.0 mL, 1.6 M, 1.6 mmol) solution was added to a cold (−78 °C) THF solution (1.0 mL) of diisopropylamine (0.224 mL, 1.6 mmol). The solution was stirred with slow warming to room temperature. After 15 min the solution was cooled to −78 °C and mesityl oxide (157 mg, 0.182 mL, 1.6 mmol) was added dropwise. The solution was then warmed to room temperature and stirred for 15 min, after which a light yellow solution was observed. The resulting (oxopentadienyl)lithium salt was slowly added dropwise to a cold (−78 °C) solution of $[Cp^*RuCl]_4$ (434 mg, 1.6 mmol) in 20 mL of THF. After the solution was warmed to room temperature and stirred for 2 h, the volatiles were removed under vacuum. Compound **1** was then extracted from the remaining residue with hexane, and the resulting solution was concentrated and then chromatographed on an Al_2O_3 (grade 1, 5 × 1.5 cm) column with a mixture of hexane/diethyl ether (8:2) as the eluant. A yellow band was collected. The solvent was removed in vacuo, and the crude product was crystallized from hexane at −78 °C to give 425 mg (1.28 mmol, 80%) of **1** as a yellow powder. Spectroscopic data were consistent with those reported previously. Single crystals were obtained by recrystallization from hexane at −15 °C.

Synthesis of Cp*Ru[η^5-$CH_2C(t\text{-}Bu)CHC(t\text{-}Bu)O$] (1′). Under a nitrogen atmosphere, a *n*-BuLi (0.70 mL, 1.6 M, 1.1 mmol) solution was added to a cold (−78 °C) THF solution (1.0 mL) of diisopropylamine (0.156 mL, 1.1 mmol). The solution was stirred with slow warming to room temperature. After 15 min the solution was cooled to −78 °C, and 2,2,5,6,6-pentamethyl-4-hepten-3-one (0.25 mL, 1.1 mmol) was added dropwise. After the solution was warmed to room temperature and stirred for 15 min, a light yellow solution was observed. The resulting (oxopentadienyl)lithium salt was slowly added dropwise to a cold (−78 °C) solution of $[Cp^*RuCl]_4$ (300 mg, 1.1 mmol) in 60 mL of THF. After the solution was warmed to room temperature and stirred for 2 h, the volatiles were removed under vacuum. Compound **1″** was then extracted from the remaining residue with diethyl ether, and the resulting solution was concentrated and then chromatographed on a 42 × 2 cm neutral alumina column with a 9:1 mixture of hexane/diethyl ether as the eluant. A yellow band was collected and, after evaporation, recrystallization from cold hexane, and filtration at −78 °C, a bright yellow solid was obtained in 88% yield (410 mg, 0.98 mmol). Mp: 68−70 °C. Crystals suitable for X-ray analysis were deposited from −5 °C hexane solutions. Anal. Calcd for $C_{22}H_{36}ORu$: C, 63.26; H, 8.72. Found: C, 63.32, H, 8.87. MS: 418(100)[M^+], 399(7), 359-(16), 331(25), 315(9), 233(42).

Synthesis of Cp*Ru[η^5-$CH_2C(Me)CHC(Me)CH_2$] (1″). To a THF solution (20 mL) containing 146 mg of $[Cp^*RuCl]_4$ (0.54 mmol) at −78 °C was added $C_7H_{11}SnMe_3$ (136 mg, 0.54 mmol) in 7 mL of THF. The addition resulted in a change in color from dark brown to yellow and then red-brown. The solution was allowed to warm slowly to room temperature and was then filtered. After removal of the volatiles, the oily residue was extracted with hexane and the solution evaporated. After chromatography under silica gel and eluting with hexane, a pale yellow solid was obtained in 79% yield (140 mg, 0.42 mmol). Spectroscopic data and physical properties have been previously reported.[1a]

Synthesis of Cp*Ru[η^3-$CH_2C(Me)CHC(Me)O$][(Cl)($SnCl_3$) (2). To a pentane solution (25 mL) containing 100 mg of compound **1** (0.30 mmol) was added 0.10 mL (221 mg, 0.85 mmol) of $SnCl_4$ with continuous stirring at room temperature. Immediately an orange precipitate was observed. After 30 min the reaction mixture was filtered and the orange residue washed twice with 20 mL portions of pentane. The solvent was removed in vacuo, and the crude product was recrystallized from CH_2Cl_2/pentane at −78 °C to give 135 mg (0.23 mmol, 76%) of **2** as a red solid, which does not melt below 250 °C. Single crystals were obtained by recrystallization from acetone at −15 °C. Anal. Calcd for $C_{16}H_{24}OCl_4SnRu$: C, 32.34; H, 4.04. Found: C, 32.70; H, 3.99. IR ($CHCl_3$, cm^{-1}): 1689(vs). MS: 330 [$M^+ - SnCl_4$].

Synthesis of Cp*Ru[η^3-$CH_2C(Me)CHC(Me)CH_2$](Cl)-($SnCl_3$) (2″). The synthesis was carried out similarly to that described for **2a″** (vide infra), but attempts to purify it were unsuccessful, and thereby prevented its isolation. Its formulation is therefore based upon NMR data (see Tables 1 and 2) of the crude reaction product.

Synthesis of Cp*Ru[η^3-$CH_2C(Me)CHC(Me)CH_2$](Cl)-($SnClMe_2$) (2a″). To a THF solution (30 mL) containing 100 mg of compound **1″** (0.35 mmol) at −78 °C was added 70 mg (0.35 mmol) of Me_2SnCl_2 with continuous stirring. After 2 h at −78 °C, the mixture was allowed to warm to room temperature and was stirred for an additional 24 h. The reaction mixture was filtered and the cherry-red residue washed three times with 3 × 5 mL hexane, leading to the extraction of **1″** from the solid. The remaining red solid was recrystallized from toluene/pentane at −78 °C to give 7 mg (0.013 mmol, 4%) of **2a″** as a red solid, which decomposes without melting at 65 °C. MS: 330 [$M^+ - SnMe_2Cl_2$]. The small quantity and low stability of **2a″** prevented its characterization by elemental analysis.

Synthesis of Cp*Ru[η^3-$CH_2C(Me)CHC(Me)O$](I_2) (3). To a hexane solution (20 mL) containing 100 mg of compound **1**

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(0.30 mmol) at −78 °C was added a toluene solution (10 mL) of 76 mg of resublimed I_2 (0.3 mmol). The yellow solution immediately became dark. The reaction mixture was left for 30 min at −78 °C and then was slowly warmed to room temperature. The solvent was removed in vacuo, and the crude product was washed twice with hexane (20 mL). Recrystallization of the dark solid from acetone/hexane gave 146 mg (0.25 mmol, 83%) of compound **3**, which did not melt below 250 °C. Anal. Calcd for $C_{16}H_{24}I_2ORu$: C, 32.7; H, 4.08; I, 43.2. Found: C, 33.0; H, 4.05; I, 41.9. IR ($CHCl_3$, cm^{-1}): 1676(vs). MS: 587(5) [M^+], 461(100), 439(25), 401(22), 385(17).

Synthesis of Cp*Ru[η^3-CH_2C(*t*-Bu)CHC(*t*-Bu)O](I)$_2$ (3′). To a hexane solution (15 mL) containing 135 mg of compound **1′** (0.33 mmol) at −78 °C was added a toluene solution (5 mL) of 82 mg of resublimed I_2 (0.33 mmol). The bright yellow solution immediately turned brown. After approximately 45 min, the reaction mixture reached room temperature, yielding a deep wine-red solution. The solvent was removed in vacuo, and the crude product was washed twice with hexane (2 × 10 mL). The product was dissolved in $CHCl_3$ and filtered. After immediate evaporation compound **3′** was obtained as a deep grape-purple solid (137 mg, 0.20 mmol, 63%), which did not melt below 250 °C. ^{1}H NMR spectroscopy always revealed the presence of the dimer $[Cp^*RuI_2]_2$ in solution in a ratio of 17:1 (**3′**:dimer). IR ($CHCl_3$, cm^{-1}): 1663(vs). MS (20 eV): 421(12), 420(53), 419(22), 418(100), 417(55), 416(44), 415(36), 412(15), 331(10), 329(11), 251(67), 180(20), 166(10), 165(77), 125(29), 124(49), 57(30). HRMS: [M − I_2] 418.1803; found 418.1802.

Synthesis of Cp*Ru[η^3-CH_2C(Me)CHC(Me)CH_2](I)$_2$ (3″). To a hexane solution (20 mL) containing 100 mg of compound **1″** (0.30 mmol) at −78 °C was added a toluene solution (10 mL) of 76.6 mg of resublimed I_2 (0.35 mmol). The yellow solution immediately became dark. The reaction mixture was kept for 30 min at −78 °C, and then on warming slowly to room temperature it went from red-brown to wine-red. The solvent was removed in vacuo, and the crude product was washed twice with hexane (2 × 10 mL). Recrystallization of the wine-red solid from acetone gave 142 mg (0.25 mmol, 81%) of deep wine-red **3″**, which decomposes without melting at 160 °C. Anal. Calcd for $C_{17}H_{26}I_2Ru$: C, 34.89; H, 4.44; I, 43.38. Found: C, 34.91; H, 4.33; I, 42.91. IR ($CHCl_3$, cm^{-1}): 1600-(C═C, w). LRFAB (matrix 3-NBA): 332 [M^+].

Synthesis of Cp*Ru[η^3-CH_2C(Me)CHC(Me)O](Cl)$_2$ (4). A light yellow chloroform solution (20 mL) containing 100 mg of compound **1** (0.30 mmol) was refluxed for 2 h, whereupon it became dark brown. After filtration and evaporation of the solvent, the amber residue was purified by thin-layer chromatography, using silica gel and $CHCl_3$ as eluent. There were five bands, and the two most intense orange bands were separated and extracted with chloroform, giving 25 mg and 6 mg of the corresponding amber isomers **4na** (0.06 mmol, 18%) and **4xs** (0.014 mmol, 4%). Both samples did not melt even at 250 °C. Anal. Calcd for **4na**: $C_{16}H_{24}Cl_2ORu$: C, 47.52; H, 5.94; Cl, 17.57. Found: C, 47.75; H, 6.16; Cl, 17.06. IR ($CHCl_3$, cm^{-1}): **4na** 1664(vs), **4xs** 1692(vs). MS for **4na**: 404(1.3) [M^+], 369-(7.5), 334(100), 302(46), 289(27), 236(67), 97(91).

Synthesis of Cp*Ru[η^3-CH_2C(*t*-Bu)CHC(*t*-Bu)O](Cl)$_2$ (4′). A chloroform solution (30 mL) containing 300 mg of compound **1′** (0.72 mmol) was maintained at reflux for 8 h. The light yellow solution turned dark green. After filtration and evaporation of the solvent, the green oily residue was washed twice with pentane (2 × 10 mL). The pentane-insoluble fraction was dissolved in dry EtOH (10 mL), and an orange precipitate was immediately observed. After filtration, the orange powder was washed with EtOH (∼35 mL) until the washings were no longer green. The orange solid **4na′** was obtained (88 mg, 0.18 mmol, 25%) and decomposes without melting at 180 °C. The green ethanolic solution was purified through chromatographic separation on an alumina column with elution by EtOH. A green band was collected and its volume was reduced (∼2 mL) by evaporation under vacuum. After addition of hexane (∼8 mL) ca. 45 mg of a green solid was isolated by filtration.[30] **4na′**: IR ($CHCl_3$, cm^{-1}): 1666(vs). HRMS: calc for $C_{22}H_{36}Cl_2ORu$, 488.1180; found 488.1165; [M − Cl_2]: 418.1803, found 418.1800.

Synthesis of Cp*Ru[η^3-CH_2C(Me)CHC(Me)CH_2](Cl)$_2$ (4na″) and [Cp*Ru(η^6-C_7H_8)][Cp*RuCl$_3$] (11). A chloroform solution (30 mL) containing 100 mg of compound **1′** (0.35 mmol) was stirred for 65 h at room temperature. The light yellow solution turned yellow-brown. After filtration and evaporation of the solvent, the dark brown oily residue was extracted with Et_2O, giving an orange solution, which, after having its volume reduced to ∼15 mL, led to a mixture of yellow and dark orange precipitates of **4na″**. Attempts to purify the solid through chromatography or recrystallization were unsuccessful due to the reactivity of the mixture in solution. The fraction insoluble in Et_2O gave 30 mg of a green solid,[30] which after recrystallization from $CHCl_3$/Et_2O afforded at 5 °C a green solid, along with a few red crystals, which were removed manually. These crystals do not melt below 210 °C. An X-ray diffraction study revealed this to be compound **11**. MS for **11**: 635(24) [M^+ − Cl], 598(9.5), 545(93), 466(100), 271-(25), 236(20).

Chemical Synthesis of Cp*Ru[η^3-CH_2C(Me)CHC(Me)O]-(O_2) (5). A nitromethane solution (10 mL) containing 68 mg of compound **1** (0.20 mmol) was bubbled with pure O_2 (19.2 mg, 0.6 mmol at 297 K and 585 mm Hg), and the Schlenk vessel was closed. The initial light yellow solution turned yellow-amber after 10 min. After continuous stirring for 1.5 h at room temperature, the reaction mixture was evaporated until dryness and the amber residue extracted with Et_2O (3 × 5 mL). Filtration of the black residue, complete evaporation of the filtered amber solution, and recrystallization at room temperature from 10 mL of Et_2O, after reducing the volume until ∼2 mL, gave an amber solid **5** (42.4 mg, 0.12 mmol) after filtration in 57% yield. Mp: 110−112 °C. Single crystals were obtained by recrystallization from diethyl ether at −20 °C. IR (KBr, cm^{-1}): 1667(vs); 937(s), 894 (s). MS: 348 [M^+ − O].

Electrochemical Synthesis of Cp*Ru[η^3-CH_2C(Me)-CHC(Me)O](O_2) (5) and (η^5-C_5Me_4CHO)Ru[η^5-CH_2C(Me)-CHC(Me)O] (6).[5] The electrolysis at 0.35 V of a mixture of a 2 mM solution of compound **1** (16.7 mg) in 25 mL of MeCN and 0.1 M Bu_4NPF_6 (969 mg) was carried out until the starting material was completely consumed. Evaporation of the solvent and extractions with diethyl ether gave an oil, which was purified by chromatography on neutral alumina using diethyl ether as eluent. Evaporation of the solvent afforded 12.9 mg of compound **5** in 70% yield. If the initial reaction mixture was allowed to stand for at least 24 h, the formation of compound **6** also occurred, as observed from chromatography, carried out as described above. In this case, three bands were observed. The first was eluted with hexane, while the second and third were eluted with diethyl ether, giving compounds **1**, **5**, and **6**, respectively. Compound **6** was isolated together with another uncharacterized organometallic complex. A second chromatographic procedure for the latter mixture using neutral alumina and diethyl ether afforded pure compound **6**. Mp: 133−136 °C. Single crystals were obtained from recrystallization in diethyl ether at −15 °C. IR (CCl_4, cm^{-1}): 1670 (s). MS: 348 [M^+]. Spectroscopic data for **5** and **6** were consistent with those previously reported.

Synthesis of Cp*Ru[η^3-CH_2C(Me)CHC(Me)O]PPh_3 (7). To a cyclohexane solution (40 mL) containing 150 mg of compound **1** (0.45 mmol) was added 236 mg (0.90 mmol) of PPh_3. After the solution was refluxed 7.5 h, the solvent was removed and the yellow residue was dissolved in a minimum amount of hexane and then chromatographed on a silica gel column (5 × 1.5 cm) with a mixture of hexane/diethyl ether (9:1), leading first to recovery of starting material **1**, while a second fraction eluted with hexane/diethyl ether (8:2) afforded 35 mg of compound **7** as an orange powder (0.06 mmol, 13%). Mp: 139−143 °C. Crystals suitable for X-ray analysis were

deposited from room-temperature hexane solutions whose volumes had been reduced under vacuum. Anal. Calcd for **7**: C, 68.55; H, 6.60. Found: C, 67.94; H, 6.70. IR (KBr, cm^{-1}): 1640(s). MS: 596(2.4) [M^+], 501(6), 334(14), 252(6), 235(56), 57(100).

Synthesis of Cp*Ru[η^3-$CH_2C(Me)CHC(Me)O$]$PHPh_2$ (8). To a THF solution (250 mL) containing 250 mg of compound **1** (0.75 mmol) was added 0.13 mL (140 mg, 0.75 mmol) of $PHPh_2$. The solution was filtered into a photochemical reactor and irradiated for 4.5 h with continuous stirring. The solution changed from light yellow to orange-yellow. Filtration and evaporation of the solvent under vacuum gave an amber oil, which was extracted with diethyl ether. After the solvent was concentrated and chromatographed on a silica gel column (5 × 1.5 cm) with 1:1 hexane/diethyl ether, a mixture of compounds **1** and **8** was obtained. Several attempts to remove **1** were unsuccessful.

Synthesis of Cp*Ru[η^3-$CH_2C(Me)CHC(Me)O$]PMe_3 (9). This yellow compound was prepared in the same manner as the PPh_3 adduct (**7**), using 50 mg (0.15 mmol) of **1**, 15 mL of cyclohexane, and PMe_3 (20 μL, 0.19 mmol). The resulting yellow oil was chromatographed using pentane/diethyl ether (1:1), affording an orange band, which after reducing the solvent volume gave 43 mg (0.11 mmol, 70%). The yellow compound can be sublimed at ca. 90 °C under vacuum. Mp: 137−144 °C. Anal. Calcd for **9**: C, 55.75; H, 8.07. Found: C, 56.03; H, 8.40. IR (KBr, cm^{-1}): 1633(s). MS: 409(10) [M^+], 394-(6), 379(1), 364(1), 334(100), 302(35), 236(27).

Synthesis of Cp*Ru[η^3-$CH_2C(Me)CHC(Me)O$]CO (10). Carbon monoxide was bubbled for 10 h at atmospheric pressure into a refluxing THF solution (25 mL) containing 100 mg of compound **1** (0.3 mmol). Afterward, the solution was allowed to cool to room temperature, the solvent was removed in vacuo, and the yellow residue was chromatographed with a mixture of hexane/diethyl ether (8:2). Even though some starting material could be removed, the complete separation of compounds **10** and **1** could not be achieved. According to a ^1H NMR spectrum of the mixture, compound **10** was present approximately to the extent of 44%.

X-ray Structure Determination for 1, 1′, 2, 5−7, and 11. Crystal data and experimental details are given in Table 3. X-ray data were collected on Enraf-Nonius four-circle or rotating anode diffractometers using graphite-monochromated Mo Kα (λ = 0.7107 Å) radiation. Final positional parameters are available as Supporting Information.

Acknowledgment. M.A.P.S. and R.D.E. would like to acknowledge the support of Conacyt and National Science Foundation Bilateral Program (No. INT-9202989). M.A.P.S. would like to thank Conacyt for financial support through the project 26352-E, as well as for the X-ray diffractometer (No. F0084), and Washington University Mass Spectrometry Research Resource (NIH, No. P41RR0954) for recording some of the mass spectra. Thanks to Marco Antonio Leyva for helping us with some X-ray diffraction studies. R.D.E. would like to thank the NSF for partial support of this research.

Supporting Information Available: X-ray complementary data and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010735S