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# Synthesis and Structural Characterization of $\eta^6$ -Arene Ruthenium Complexes Bearing Pentadienyl and Oxopentadienyl Ligands

Armando Ramirez-Monroy,<sup>‡</sup> M. Angeles Paz-Sandoval,<sup>\*,‡</sup> Michael J. Ferguson,<sup>†</sup> and Jeffrey M. Stryker<sup>\*,§</sup>

Departamento de Quimica, Cinvestav, Avenida IPN # 2508 Col. San Pedro Zacatenco, C. P. 07360, Mexico, D.F., Mexico, Department of Chemistry, Structure Determination Laboratory, University of Alberta, Edmonton, Alberta T6G 2G2, Canada, and Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada

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General methodology for the synthesis of cationic ruthenium(II)  $\eta^5$ -pentadienyl compounds stabilized by the  $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}$  fragment has been developed. Pentadienyl compounds  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{\eta^5\text{-CH}_2\text{C}(\text{R}_2)\text{CHC}(\text{R}_4)\text{CH}(\text{R}_5)\}]\text{BF}_4$  ( $\text{R}_2 = \text{R}_4 = \text{R}_5 = \text{H}$ , **2-BF**<sub>4</sub>;  $\text{R}_2, \text{R}_4 = \text{H}, \text{R}_5 = \text{Me}$ , **3**;  $\text{R}_2, \text{R}_4 = \text{Me}, \text{R}_5 = \text{H}$ , **4**) can be prepared in good yields from reactions of the labile dication  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{acetone})_3](\text{BF}_4)_2$  (**1**) with 1-trimethylsilyl-2,4-pentadiene, 1-trimethylsilyl-2,4-hexadiene, and 2,4-dimethyl-1-trimethylstannyl-2,4-pentadiene, respectively. Compound **3** is isolated in 90% yield as a mixture of the *syn* and *anti* isomers. In contrast, the reaction of pentadienyllithium with  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  provides a nonselective reaction, which affords a mixture of isomeric  $\eta^1$ -,  $\eta^3$ -, and  $\eta^5$ -coordinated pentadienyl complexes,  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-CH}_2\text{CHCHCHCH}_2)]\text{Cl}$  (**2-Cl**),  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-CH}_2\text{CHCHCH}=\text{CH}_2)]\text{Cl}$  (**5**), and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^1\text{-CH}_2\text{CH}=\text{CHCH}=\text{CH}_2)]\text{Cl}_2$  (**6**); the reaction of 1,4-pentadiene and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  in ethanolic carbonate similarly gives a mixture containing complex **5**,  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{\eta^3\text{-C}(\text{Me})\text{CHC}(\text{Me})\}\text{Cl}]$  (**7**), and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-CH}_2\text{CHCHCH}_2\text{Me})\text{Cl}]$  (**8**). Using a similar strategy for the synthesis of the corresponding oxopentadienyl derivatives is much more complicated, even when using an enol silane as the nucleophilic precursor, reflecting a greater competition among alternative bonding modes for the oxopentadienyl derivatives compared to the corresponding pentadienyl analogues. The reaction of lithium oxopentadienide and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  in THF affords  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-exo-syn-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})\text{Cl}]$  (**11**) in poor yield, although this complex readily affords  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-exo-syn-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})]\text{BF}_4$  (**9**) upon reaction with silver tetrafluoroborate. The analogous  $\eta^6$ -benzene complex,  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\eta^3\text{-exo-syn-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})\text{Cl}]$  (**13**), can be prepared, albeit in very low yield, in an analogous manner to that reported for complex **11**, along with traces of an isomeric congener, **13-endo**. The use of 1-trimethylsilyloxy-1,3-butadiene unexpectedly provided strongly contrasting results upon addition to dicationic complex **1**, returning a mixture of  $\eta^5$ - and  $\eta^3$ -oxopentadienyl complexes  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-CH}_2\text{CHCHCHO})]\text{BF}_4$  (**14**) and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(1\text{-3,5-}\eta\text{-exo-syn-CH}_2\text{CHCHCHO})]_2(\text{BF}_4)_2$  (**15**). Addition of water to the dimeric product **15** affords the monomeric aquo adduct  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-exo-syn-CH}_2\text{CHCHCHO})(\text{H}_2\text{O})]\text{BF}_4$  (**16**), but this complex is unstable toward isolation, reverting back to dimer **15** upon precipitation. A more stable adduct,  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-exo-syn-CH}_2\text{-CHCHCHO})(\text{MeCN})]\text{BF}_4$  (**17**), is isolated upon dissolution in acetonitrile, and addition of aqueous NaCl to **15** gives compound  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-exo-syn-CH}_2\text{CHCHCHO})\text{Cl}]$  (**20**). Compound **14** affords the decarbonylation product  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-allyl})(\text{CO})]\text{BF}_4$  (**19**) as a mixture of *exo* and *endo* allyl isomers. The solid-state structures for compounds **2-BF**<sub>4</sub>, **4**, **9**, **11**, **13**, **15**, and **19-*exo***, as determined by X-ray crystallography, are also reported.

## Introduction

The rich chemistry of neutral  $\text{Cp}^*\text{Ru(II)}$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) pentadienyl<sup>1</sup> and heterosubstituted pentadienyl complexes<sup>2</sup> raises considerable interest in the corresponding chemistry of the isoelectronic but cationic  $\eta^6$ -arene ruthenium(II) complexes. The reactivity of “half-open” ruthenocene  $\eta^5$ -pentadienyl and  $\eta^5$ -oxopentadienyl complexes toward exogenous ligand coordination, oxidative addition, and coupling reactions with unsaturated substrates is strongly influenced by the electronic

and steric properties of both the metal and the ancillary ligands.<sup>3</sup>

A comparative investigation into the reactivity of the cationic  $\eta^6$ -arene analogues thus provides an important assessment of electronic factors that control the products of such reactions.

Open pentadienyl complexes of ruthenium supported by an ancillary arene ligand constitute a relatively new class of mixed

\* To whom correspondence should be addressed. E-mail: jeff.stryker@ualberta.ca; mpaz@cinvestav.mx.

<sup>‡</sup> Cinvestav.

<sup>†</sup> Structure Determination Laboratory, University of Alberta.

<sup>§</sup> Department of Chemistry, University of Alberta.

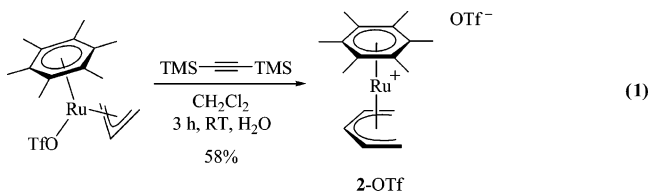
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sandwich complexes. Relevant complexes of the general formula  $[(\eta^6\text{-arene})\text{Ru}(\eta^5\text{-dienyl})]^+$  have been prepared for a range of endocyclic  $\eta^5$ -dienyl ligands, but among acyclic systems, only the 2,4-dimethyl- $\eta^5$ -pentadienyl ligand has been published and investigated. No heterosubstituted  $\eta^5$ -oxopentadienyl complexes have as yet been reported.

A range of procedures have been developed for the synthesis of mixed sandwich  $(\eta^6\text{-arene})\text{ruthenium}$  pentadienyl complexes, most of which cannot be readily generalized. Protonation of the zerovalent cyclic tetraene or triene complexes  $[(\eta^6\text{-arene})\text{-Ru}(\eta^4\text{-COT})]^{4a}$  (arene = benzene, mesitylene, hexamethylbenzene, *tert*-butylbenzene, COT = cyclooctatetraene) and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^4\text{-C}_7\text{H}_8)]^{4b}$  is reasonably general, using strong acid to provide the corresponding  $\eta^5$ -cyclooctatrienyl and  $\eta^5$ -cycloheptadienyl cations,  $[(\eta^6\text{-arene})\text{-Ru}(\eta^5\text{-C}_8\text{H}_9)]^+$  and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-C}_7\text{H}_9)]^+$ , respectively.<sup>4</sup> Silver-assisted ionization of  $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$  in the presence of a cyclic diene or triene (e.g., cyclopentadiene, pentamethylcyclopentadiene, 1,3-cyclohexadiene, 1,3-cycloheptadiene, 1,5-cyclooctadiene, and 1,3,5-cycloheptatriene) under ultrasonic irradiation also produces the corresponding cationic complexes,  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\eta^5\text{-cyclo-dienyl})]\text{BF}_4$ , by a process that presumably involves spontaneous deprotonation.<sup>5</sup> Complexation and solvent-mediated deprotonation of dienes (e.g., 1,3-cyclooctadiene, 2,4-dimethyl-1,3-pentadiene, and cyclopentadiene) in the presence of  $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$  and a suitable arene in ethanol gives a series of cationic complexes  $[(\eta^6\text{-arene})\text{Ru}(\eta^5\text{-dienyl})]^+$ , although for acyclic dienes, alkyl substitution is essential to inhibit competitive diene polymerization.<sup>6</sup> Similarly, protonation of the open-ruthenocene complex  $[\text{Ru}(2,4\text{-dimethyl-}\eta^5\text{-pentadienyl})_2]^7$  with  $\text{HBF}_4$  in the presence of excess arene leads to the formation of  $[(\eta^6\text{-arene})\text{Ru}(2,4\text{-dimethyl-}\eta^5\text{-pentadienyl})]\text{BF}_4$  (arene = benzene, *p*-xylene).<sup>8</sup> In the presence of base, dimeric di- $\mu$ -chlorodichlorobis $[(1-3\eta:6-8\eta)\text{-2,7-dimethyloctadienediyl}]\text{diruthenium(IV)}$  reacts with both cyclic and acyclic dienes to give the corresponding bis( $\eta^5$ -dienyl)ruthenium(II) compounds, which can be further transformed by protonation and ligand exchange with added arene, as described above.<sup>9</sup>

Most recently, the unsubstituted acyclic  $\eta^5$ -pentadienyl ruthenium complex  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-pentadienyl})]\text{OTf}$  (**2-OTf**) was unexpectedly obtained in moderate yield from the reaction of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-allyl})]\text{OTf}$  with bis(trimethylsilyl)ethyne (eq 1).<sup>10</sup> Similar reactions conducted using a range of other disubstituted alkynes proceed instead by concomitant oxidative cyclization of the allyl and alkyne ligands with protolytic demethylation of the ancillary ligand to yield methane and the disubstituted cyclopentadienyl complexes  $[(\eta^6\text{-C}_6\text{Me}_5\text{H})\text{Ru}(\eta^5\text{-$

1,2-dialkylcyclopentadienyl)]OTf.<sup>11</sup> The reaction is clearly diverted to acyclic products by the presence of the trimethylsilyl substituents; isotopic labeling experiments with deuterated water confirm that the silyl substituents are ultimately lost by adventitious protodesilylation.



As an extension of our investigations of half-open ruthenocene chemistry,<sup>3a</sup> we therefore sought a rational high-yield synthesis for acyclic ruthenium pentadienyl and heteropentadienyl complexes supported by an ancillary hexamethylbenzene ligand, which could not be prepared using methodology adapted from the corresponding  $\text{Cp}^*\text{Ru}$  series. The reactivity of the  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{heterodienyl})]^+$  series, in particular, will provide an instructive comparison to the pentadienyl and oxopentadienyl/alkyne coupling reactions reported for the isoelectronic, but neutral,  $\text{Cp}^*\text{Ru}(\text{heterodienyl})$  derivatives.<sup>3b</sup>

Herein we report a general synthesis of half-open ruthenocene complexes of the form  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-pentadienyl})]^+$ , as well as both neutral and cationic hexamethylbenzene derivatives containing the first examples of  $\eta^5$ - and  $\eta^3$ -coordinated oxopentadienyl ligands.

## Results and Discussion

**A. Synthesis and Spectroscopy of  $\eta^5$ -Pentadienyl Compounds.** Cationic  $\eta^5$ -pentadienyl compounds  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{\eta^5\text{-CH}_2\text{C(R}_2\text{)CHC(R}_4\text{)CH(R}_5\text{)}\}]\text{BF}_4$  ( $\text{R}_2 = \text{R}_4 = \text{R}_5 = \text{H}$ , **2-BF**<sub>4</sub>;  $\text{R}_2 = \text{R}_4 = \text{H}$ ,  $\text{R}_5 = \text{Me}$ , **3**;  $\text{R}_2 = \text{R}_4 = \text{Me}$ ,  $\text{R}_5 = \text{H}$ , **4**) are isolated from reactions of the labile dication  $[(\eta^6\text{-C}_6\text{Me}_6)\text{-Ru}(\text{acetone})_3](\text{BF}_4)_2$  (**1**)<sup>12</sup> with 1-trimethylsilyl-2,4-pentadiene,<sup>13a</sup> 1-trimethylsilyl-2,4-hexadiene,<sup>13b</sup> and 2,4-dimethyl-1-trimethylstannyl-2,4-pentadiene, respectively (Scheme 1). The reactions proceed very slowly at room temperature, but high yields and convenient reaction times are obtained by heating the reaction mixtures to reflux in acetone. Compounds **2-BF**<sub>4</sub> and **4** are obtained as exclusive products in 85% and 83% yields, respectively, while compound **3** is isolated in 90% yield as a mixture of the *syn* and *anti* isomers in a 3:1 ratio, respectively, as determined by <sup>1</sup>H NMR spectroscopy. Although we presume that the corresponding 2,4-dimethyl-1-trimethylsilyl-2,4-pentadiene would also proceed to give pentadienyl compound **4**, the stannyl derivative was conveniently available to us and demonstrates additional flexibility in this general synthetic strategy.

Square yellow crystals of the *syn* isomer **3-syn** can be obtained from the product mixture by successive recrystallizations from acetone/diethyl ether, while the corresponding *anti* isomer, **3-anti**, can be obtained only as a mixture with **3-syn**. However, a small amount of the pure *anti* isomer was isolated by fractional crystallization as thin yellowish needles, providing infrared spectroscopy and mass spectrometry of each compound as a single isomer. X-ray crystal structure determinations were conducted for complexes **2-BF**<sub>4</sub> (Figure 1) and **4** (Figure 2),

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**Table 1.**  $^1\text{H}$  NMR Data<sup>a</sup> for Compounds 2–8

compound	H1( <i>anti</i> )	H1( <i>syn</i> )	H2	H3	H4	H5	C <sub>6</sub> Me <sub>6</sub>
<b>2-BF<sub>4</sub></b>	1.19 (ddd) $J_{\text{H1a,H1s}} = 2.9$ $J_{\text{H1a,H2}} = 10.5$ $^4J = 0.8$	2.95 (dd) $J_{\text{H1a,H1s}} = 2.9$ $J_{\text{H1s,H2}} = 8.6$	4.91 (tdd, br) $J_{\text{H2,H3}} = 6.1$ $J_{\text{H2,H1}} = 9.6$ $^4J = 0.7$	5.94 (tt) $J_{\text{H2,H3}} = 6.1$ $^4J = 0.8$			2.40 (s)
<b>2-Cl</b>	0.45 (dd) $J_{\text{H1a,H1s}} = 2.5$ $J_{\text{H1a,H2}} = 8.7$ 0.78 (dd) <sup>b</sup> $J_{\text{H1a,H1s}} = 2.5$ $J_{\text{H1a,H2}} = 8.7$ $J_{\text{H1a,H1s}} = 3.3$ $J_{\text{H1a,H2}} = 10.1$	2.30 (dd) $J_{\text{H1a,H1s}} = 2.5$ $J_{\text{H1s,H2}} = 8.5$ 2.44 (dd) $J_{\text{H1a,H1s}} = 2.5$ $J_{\text{H1s,H2}} = 8.5$ $J_{\text{H1a,H1s}} = 3.3$ $J_{\text{H1s,H2}} = 8.9$	4.10 (dt) $J_{\text{H2,H3}} = 6.0$ $J_{\text{H2,H1}} = 8.5, 9.0$ 3.98 (dt) $J_{\text{H2,H3}} = 5.5$ $J_{\text{H2,H1}} = 8.5, 9.0$ 4.68 (td) $J_{\text{H2,H3}} = 6.2$ $J_{\text{H2,H1}} = 9.5$	4.72 (t) $J_{\text{H2,H3}} = 6.0$  4.48 (t) $J_{\text{H2,H3}} = 6.0$   5.78 (td) $J_{\text{H2,H3}} = 6.2$ $^4J = 0.6$			1.80 (s) or 1.45 (s) <sup>d</sup>  1.61 or 1.45 <sup>d</sup>
<b>3-<i>syn</i></b>	1.20 (dd) $J_{\text{H1a,H1s}} = 3.3$ $J_{\text{H1a,H2}} = 10.1$	2.85 (dd) $J_{\text{H1a,H1s}} = 3.3$ $J_{\text{H1s,H2}} = 8.9$	4.68 (td) $J_{\text{H2,H3}} = 6.2$ $J_{\text{H2,H1}} = 9.5$	5.78 (td) $J_{\text{H2,H3}} = 6.2$ $^4J = 0.6$	4.94 (dd) $J_{\text{H3,H4}} = 6.1$ $J_{\text{H4,H5}} = 9.9$	1.72 (dq, H <sub>5a</sub> ) $J_{\text{H4,H5a}} = 9.9$ $J_{\text{H5a,Me5s}} = 6.1$ 1.50 (d, Me <sub>5a</sub> ) $J_{\text{H5a,Me5s}} = 6.1$ 3.40 (dq, H <sub>5s</sub> ) $J_{\text{H4,H5s}} = 8.3$ $J_{\text{H5s,Me5a}} = 6.8$ 0.62 (d, Me <sub>5a</sub> ) $J_{\text{H5s,Me5a}} = 6.8$	2.36 (s)
<b>3-<i>anti</i></b>	1.68 (ddq) $J_{\text{H1a,H1s}} = 3.4$ $J_{\text{H1a,H2}} = 9.7$ $^4J = 0.8$	2.93 (dd) $J_{\text{H1s,H1a}} = 3.4$ $J_{\text{H1s,H2}} = 8.8$	4.92 (ddd) $J_{\text{H1s,H2}} = 8.8$ $J_{\text{H1a,H2}} = 9.7$ $J_{\text{H2,H3}} = 6.7$	6.08 (t, br) $J_{\text{H2,H3}} = 6.6$ $J_{\text{H3,H4}} = 6.2$	4.67 (ddd) $J_{\text{H3,H4}} = 6.2$ $J_{\text{H4,H5}} = 8.3$ $^4J = 0.7$	3.40 (dq, H <sub>5s</sub> ) $J_{\text{H4,H5s}} = 8.3$ $J_{\text{H5s,Me5a}} = 6.8$ 0.62 (d, Me <sub>5a</sub> ) $J_{\text{H5s,Me5a}} = 6.8$	2.35 (s)
<b>4</b>	1.09 (d) $J_{\text{H1a,H1s}} = 3.3$	2.80 (d) $J_{\text{H1a,H1s}} = 3.0$	1.98 (s)	5.85(s)			2.34 (s)
<b>4'</b>	−0.10 (d) $J_{\text{H1a,H1s}} = 2.0$	1.94 (d) $J_{\text{H1a,H1s}} = 2.0$	1.76 (s) <sup>c</sup>	4.87 (s)			1.77 (s, Cp*)
<b>5</b>	2.20 (d) $J_{\text{H1a,H2}} = 10.5$  2.91 (dd) <sup>b</sup> $J_{\text{H1a,H2}} = 10.7$ $^4J = 1.0$	3.08 (d) $J_{\text{H1s,H2}} = 6.5$  3.00 (d) $J_{\text{H1s,H2}} = 6.8$	3.73 (td) $J_{\text{H1s,H2}} = 6.5$ $J_{\text{H1a,H2}} = 10.5$  3.30 (td) $J_{\text{H1s,H2}} = 6.8$ $J_{\text{H1a,H2}} = 10.4, 10.6$	3.61 (t) $J_{\text{H2,H3(H4)}} = 10.0, 10.5$  4.31 (t) $J_{\text{H2,H3(H4)}} = 10.2$	5.92 (dt) $J_{\text{H3,H4}} = 10.0$ $J_{\text{H4,H5trans}} = 17.0$  5.68 (dt) $J_{\text{H3,H4}} = 10.0, 10.2$ $J_{\text{H4,H5trans}} = 17.0$	5.09 (dd, H <sub>5trans</sub> ) $J_{\text{H5cis,H5trans}} = 2.0$ $J_{\text{H4,H5trans}} = 16.7$ 5.25 (dd, H <sub>5cis</sub> ) $J_{\text{H5cis,H5trans}} = 2.0$ $J_{\text{H4,H5cis}} = 9.7$ 5.33 (ddd, H <sub>5trans</sub> ) $J_{\text{H5cis,H5trans}} = 2.0$ $J_{\text{H4,H5trans}} = 17.0$ $^4J = 0.6$ 5.25 (ddd, H <sub>5cis</sub> ) $J_{\text{H5cis,H5trans}} = 2.0$ $J_{\text{H4,H5cis}} = 10.2$ $^4J = 0.6$	1.98 (s)   1.58 (s)
<b>6</b>	4.86 (dd, H <sub>1cis</sub> ) $J_{\text{H1cis,H1trans}} = 2.0$ $J_{\text{H2,H1cis}} = 10.0$ 4.92 (dd, H <sub>1cis</sub> ) <sup>b</sup> $J_{\text{H1cis,H1trans}} = 1.5$ $J_{\text{H2,H1cis}} = 10.0$ 3.39 (dq, H <sub>1a</sub> ) <sup>b</sup> $J_{\text{H1a,Me1}} = 6.8$ $J_{\text{H1a,H2}} = 10.0$	5.00 (dd, H <sub>1trans</sub> ) $J_{\text{H1cis,H1trans}} = 2.0$ $J_{\text{H2,H1trans}} = 17.0$ 5.06 (dd, H <sub>5trans</sub> ) $J_{\text{H1cis,H1trans}} = 1.5$ $J_{\text{H2,H1trans}} = 17.0$ 1.49 (d, Me <sub>1s</sub> ) $J_{\text{H1a,Me1}} = 6.4$	6.26 (dt) $J_{\text{H2,H1cis(H3)}} = 10.0, 10.5$ $J_{\text{H2,H1trans}} = 17.0$ 6.31 (dt) $J_{\text{H2,H1cis(H3)}} = 10.0, 10.5$ $J_{\text{H2,H1trans}} = 17.0$ 2.98 (t) $J_{\text{H1a,H2}} = 10.0$	5.80 (dd) $J_{\text{H3,H2}} = 10.0, 10.5$ $J_{\text{H4,H3}} = 15.2$ 5.90 (dd) $J_{\text{H3,H2}} = 10.5$ $J_{\text{H4,H3}} = 15.0$	5.49 (dt) $J_{\text{H5,H4}} = 8.0$ $J_{\text{H4,H3}} = 15.0$ 5.50 (dt) $J_{\text{H5,H4}} = 7.5, 8.0$ $J_{\text{H4,H3}} = 15.0$	1.40 (d) $J_{\text{H5,H4}} = 8.0$  ~1.47 <sup>c</sup>	1.80 (s) or 1.45 (s) <sup>d</sup>  1.61(s) or 1.45 (s) <sup>d</sup>
<b>7</b>	3.39 (dq, H <sub>1a</sub> ) <sup>b</sup> $J_{\text{H1a,Me1}} = 6.8$ $J_{\text{H1a,H2}} = 10.0$	1.49 (d, Me <sub>1s</sub> ) $J_{\text{H1a,Me1}} = 6.4$	2.98 (t) $J_{\text{H1a,H2}} = 10.0$				1.62(s)
<b>8</b>	2.76 (dd) <sup>b</sup> $J_{\text{H1a,H2}} = 10.4$ $^4J = 1.0$	2.93 (d) $J_{\text{H1s,H2}} = 6.7$	3.04 (dt) $J_{\text{H1a,H2}} = 10.4$ $J_{\text{H1s,H2}} = 6.6$	3.50 (dt) $J_{\text{H2,H3}} = 9.7$ $J_{\text{H3,H4}} = 4.7$	1.90 (m) 1.44 (m)	1.12 (t, Me5) $J_{\text{H4,H5}} = 7.3$	1.63 (s)

<sup>a</sup> For numbering see corresponding schemes. (CD<sub>3</sub>)<sub>2</sub>CO,  $\delta$ ,  $J$  = coupling constant in Hz; (s) singlet; (d) doublet; (t) triplet; (q) quartet; (m) multiplet; (br) broad. <sup>b</sup>In C<sub>6</sub>D<sub>6</sub>. <sup>c</sup>Overlapped signal. <sup>d</sup>Assignment could be reversed.

**Table 2.**  $^{13}\text{C}$  NMR Data<sup>a</sup> for Compounds 2–8

compound	C1	C2	C3	C4	C5	R2, R4 or R5	C <sub>6</sub> Me <sub>6</sub>	C <sub>6</sub> Me <sub>6</sub>
<b>2-BF<sub>4</sub></b>	54.33	92.38	96.90				105.27	16.65
<b>3-<i>syn</i></b>	55.28	91.61	93.31	94.61	69.25	18.93	104.46	16.55
<b>3-<i>anti</i></b>	53.64	92.27	100.70	88.49	58.30	17.44	105.66	16.27
<b>4</b>	53.55	104.46	95.56			23.69	104.89	16.45
<b>4'</b>	44.69	91.83	92.51			25.72	90.10 (Cp*)	10.77 (Cp*)
<b>5</b>	51.93 <sup>b</sup>	89.04	72.71	140.83	112.20		95.55	14.97
<b>7</b>	64.24 <sup>b</sup>							
	17.92(Me)	90.90					95.50	15.32
<b>8</b>	52.08 <sup>b</sup>	88.63	75.52	26.50	16.99		95.67	15.26

<sup>a</sup> For numbering see corresponding schemes. (CD<sub>3</sub>)<sub>2</sub>CO,  $\delta$ . <sup>b</sup>In C<sub>6</sub>D<sub>6</sub>.

which crystallize from acetone/diethyl ether at low temperature and acetone at room temperature, respectively (*vide infra*).

Both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy provide clear evidence of  $\eta^5$ -coordination for the pentadienyl ligands (Tables 1 and 2).

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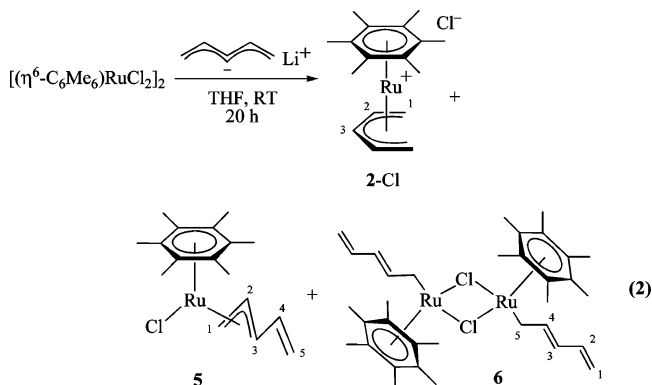
The methyl groups of the coordinated hexamethylbenzene ligands appear around  $\delta$  2.30 in the  $^1\text{H}$  NMR spectra and  $\delta$  16.0 in the  $^{13}\text{C}$  NMR spectra.<sup>4a,14</sup> A characteristic upfield chemical shift is observed in the  $^1\text{H}$  NMR spectrum for the terminal *anti* hydrogen of the  $\eta^5$ -pentadienyl moiety ( $\delta$  0.45–1.68), contrasting the more downfield resonance of the geminal



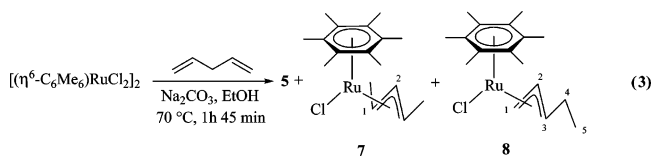
*syn* hydrogen ( $\delta$  2.30–2.93); the hydrogen at the pentadienyl central carbon is consistently the most deshielded resonance, appearing at  $\delta$  4.10–4.92. Compounds **2-BF<sub>4</sub>** and **3** show pentadienyl chemical shifts closely analogous to those observed in the corresponding  $\eta^5$ -cycloheptadienyl complexes  $[(\eta^6\text{-arene})\text{-Ru}(\eta^5\text{-C}_8\text{H}_9)]^+$  (arene = hexamethylbenzene, mesitylene, *tert*-butylbenzene),<sup>4a</sup>  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\eta^5\text{-cycloheptadienyl})]^+$  (cycloheptadienyl = cyclohexadienyl, cycloheptadienyl),<sup>5</sup> and  $[(\eta^6\text{-C}_7\text{H}_7\text{SO}_3)\text{Ru}(\eta^5\text{-C}_8\text{H}_9)]$ ,<sup>6</sup> while the NMR spectroscopic data for the 2,4-dimethyl- $\eta^5$ -pentadienyl ligand of compound **4** show the same general pattern of resonances as that found for the closely related  $[(\eta^6\text{-arene})\text{Ru}(2,4\text{-dimethyl-}\eta^5\text{-pentadienyl})]^+$  complexes (arene = *p*-toluenesulfonate, benzene, *p*-xylene, toluene).<sup>6,8,9</sup> Compared to the isoelectronic neutral complex  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(2,4\text{-dimethyl-}\eta^5\text{-pentadienyl})]$  (**4'**),<sup>3a,1b,15</sup> (see Table 1), the chemical shifts of the 2,4-dimethyl- $\eta^5$ -pentadienyl ligand in **4** are shifted to higher frequency (Table 1), but appear at lower frequency compared to the cationic complexes of the group 9 metals,  $[(\eta^5\text{-C}_5\text{R}_5)\text{Co}(2,4\text{-dimethyl-}\eta^5\text{-pentadienyl})]\text{BF}_4$  (R = H,<sup>16</sup> Me<sup>17</sup>),  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Rh}(2,4\text{-dimethyl-}\eta^5\text{-pentadienyl})]\text{BF}_4$ ,<sup>1e</sup> and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(2,4\text{-dimethyl-}\eta^5\text{-pentadienyl})]\text{BF}_4$ ,<sup>18</sup> suggesting that the ruthenium complex is inherently more electron rich (Table 1). To the extent that such qualitative cross-comparisons can be made, the  $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}^+$  fragment appears to be less electrophilic than the corresponding  $\eta^5\text{-Cp}^*\text{M}^+$  (M = Co, Rh, Ir) fragments (*vide infra*).

A range of alternative synthetic procedures previously used for the synthesis of the corresponding neutral  $\text{Cp}^*\text{Ru}(\text{pentadienyl})$  complexes,<sup>1b</sup> as well as some methods applied to the synthesis of related  $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}$  diene and allyl complexes,<sup>19</sup> proved to be unselective in the cationic  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-pentadienyl})]^+$  series. Thus, the reaction of pentadienyllithium with  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  in tetrahydrofuran proceeds after 20 h at room temperature to a mixture consisting mostly of unreacted starting material, along with liberated hexamethylbenzene and at least four minor pentadienyl complexes, as determined by <sup>1</sup>H NMR analysis. Three of the minor products were unambiguously identified by <sup>1</sup>H NMR spectroscopy, providing isomeric  $\eta^1$ -,  $\eta^3$ -, and  $\eta^5$ -coordinated pentadienyl complexes,  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-CH}_2\text{CHCHCHCH}_2)]\text{Cl}$  (**2-Cl**),  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-CH}_2\text{CHCHCH}=\text{CH}_2)]\text{Cl}$  (**5**), and the dimer  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^1\text{-CH}_2\text{CH}=\text{CHCH}=\text{CH}_2)]_2$  (**6**), in a 5:2:5 ratio, respectively (Table 1, eq 2). Chromatography of the crude reaction mixture on silica gel, followed by trituration with pentane and ether, afforded an insoluble yellow powder spectroscopically identified as the  $\eta^3$ -pentadienyl isomer **5**. The soluble fraction was similarly determined to be a mixture of **2-Cl** and **6**, along with residual traces of **5**, but this mixture could not be further separated (see Experimental Section). Complex **2-Cl** provides NMR spectra similar to those obtained from complex **2-BF<sub>4</sub>** and can be quantitatively converted to the fully characterized tetrafluoroborate salt (*vide infra*). When heated to 70 °C for 24 h in C<sub>6</sub>D<sub>6</sub>, the mixture of **2-Cl**, **5**, and **6** shows evidence only of decomposition; the relative ratio of the products remains constant. Addition of excess AgBF<sub>4</sub> to the isomeric mixture,

however, leads to quantitative formation of the expected product,  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-CH}_2\text{CHCHCHCH}_2)]\text{BF}_4$  (**2-BF<sub>4</sub>**), exclusively.



The reaction of 1,4-pentadiene with  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  in ethanolic carbonate gives a red solution consisting of free hexamethylbenzene and three organometallic complexes:  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-CH}_2\text{CHCHCH}=\text{CH}_2)]\text{Cl}$  (**5**),  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(1,3\text{-dimethyl-}\eta^3\text{-allyl})]\text{Cl}$  (**7**), and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(3\text{-ethyl-}\eta^3\text{-allyl})]\text{Cl}$  (**8**) in a ratio of 1:3:6, respectively (eq 3, Tables 1 and 2). Complexes **7** and **8** are hydrogenation products, possibly arising from “disproportionation” of the diene mediated by  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\mu\text{-H})_2(\mu\text{-Cl})\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)]\text{Cl}$ , which is produced in the initial reaction mixture.<sup>19</sup> The latter is known to react with an alkene to give the alkane and the corresponding  $\eta^3$ -allylruthenium(II) or dieneruthenium(0) complexes.<sup>19</sup>



No reaction is observed between  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  and 1-trimethylsilyl-2,4-pentadiene, either as a solution in CH<sub>2</sub>Cl<sub>2</sub> or as a suspension in MeCN at reflux. This contrasts with typical  $\text{Cp}^*\text{Ru}$  chemistry, where the Ru(IV) and Ru(II) adducts  $[\text{Cp}^*\text{Ru}(\eta^3\text{-exo-CH}_2\text{CHCHCH}=\text{CH}_2)]_2$ ,  $[\text{Cp}^*\text{Ru}(\eta^3\text{-exo-CH}_2\text{CHCHCH}=\text{CHSiMe}_3)]_2$ , and  $[\text{Cp}^*\text{Ru}(\eta^4\text{-CH}_2\text{CH}=\text{CHCH}=\text{CHCH}_2\text{SiMe}_3)]\text{Cl}$  are obtained in good yield under very mild conditions starting from  $[\text{Cp}^*\text{RuCl}_2]_2$  and  $[\text{Cp}^*\text{RuCl}]_4$ .<sup>20</sup>

Finally, oxidative addition of 3-bromo-1,5-hexadiene to  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{CH}_2=\text{CH}_2)_2]$ <sup>21</sup> leads only to an insoluble red powder, which has eluded purification and characterization. Mass spectrometry (electrospray) indicates that the product has a high molecular weight ( $m/z$  = 704.9 and 766.8), suggestive of one or more polynuclear products.

**B. Synthesis and Spectroscopy of Oxopentadienyl Compounds.** The corresponding oxopentadienyl complex  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(2,4\text{-dimethyl-}\eta^5\text{-oxopentadienyl})]\text{BF}_4$  (**9**) can be prepared using a similar synthetic procedure to that described for the pentadienyl analogues. Thus, the reaction of the dication **1**, prepared *in situ*, with a mixture of isomeric dienol silanes (major component: 1,3-dimethyl-1-trimethylsilyloxy-1,3-butadiene) proceeds under mild conditions, leading to the isolation of oxopentadienyl complex **9** after purification by repeated silica gel chromatography (Scheme 2). Initial elution using CH<sub>2</sub>Cl<sub>2</sub>/

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**Table 3.**  $^1\text{H}$  NMR Data<sup>a</sup> for Compounds 9–11 and 13–20

compound	H1 <i>anti</i>	H1 <i>syn</i>	H2 or Me6	H3	H4 or Me5	C <sub>6</sub> Me <sub>6</sub>
<b>9</b>	2.29 (s) <sup>b</sup>	3.95 (s)	1.87 (s)	5.89 (s)	2.29 (s)	2.35 (s)
<b>10</b>	0.81 (d) $J_{\text{H1a,H1s}} = 3.4$	2.65 (dd) $J_{\text{H1a,H1s}} = 3.4$ $^4J = 0.5$	2.00 (s)	5.65 (s)	0.93 (d, H <sub>5a</sub> ) $J_{\text{H5a,H5s}} = 5.6$ 2.88 (dd, H <sub>5s</sub> ) $J_{\text{H5a,H5s}} = 5.5$ $^4J = 1.5$	2.28 (s)
<b>11</b>	2.39 (s) 2.95 (d) <sup>c</sup> $J_{\text{H1a,H1s}} = 1.0$	3.33 (s) 3.02 (s)	1.99 (s) 2.03 (s)	3.03 (s) 3.51 (s, br)	2.07 (s) 2.05 (s)	2.01 (s) 1.60(s)
<b>13</b>	2.17 (d) $J_{\text{H1a,H1s}} = 1.0$ 2.69 (d) <sup>c</sup> $J_{\text{H1a,H1s}} = 1.0$	2.92 (s, br) 3.31 (s, br)	2.11 (s) 1.85(s)	4.16 (s) 3.79 (s)	2.28 (s) 2.26 (s)	5.48 (s, C <sub>6</sub> H <sub>6</sub> ) 4.60 (s, C <sub>6</sub> H <sub>6</sub> )
<b>13-endo</b>	3.47 (s) <sup>c</sup>	4.04 (d) $J_{\text{H1a,H1s}} = 1.5$	1.01 (s)	4.81 (s, br)	2.19 (s)	4.57 (s, C <sub>6</sub> H <sub>6</sub> )
<b>14</b>	2.45(dq) <sup>b</sup> $J_{\text{H1a,H2}} = 11.9$ $^4J = 0.7$	4.25 (dq) $J_{\text{H1s,H2}} = 8.8$ $^4J = 0.7$	5.30 (dddd) $J_{\text{H1s,H2}} = 8.7$ $J_{\text{H1a,H2}} = 11.8$ $J_{\text{H2,H3}} = 6.2$ $^4J = 1.7$	6.0 (d, br) $J_{\text{H2,H3(H4)}} = 6.2$	7.60 (s, br)	2.45 (s)
	2.46 (dq) <sup>d</sup> $J_{\text{H1a,H2}} = 11.6$ $^4J = 0.7$	4.13 (dq) $J_{\text{H1s,H2}} = 8.9$ $^4J = 0.7$	5.08 (dddd) $J_{\text{H1s,H2}} = 8.6$ $J_{\text{H1a,H2}} = 11.8$ $J_{\text{H2,H3}} = 6.3$ $^4J = 1.7$	5.76 (d,br) $J_{\text{H2,H3(H4)}} = 6.2$	7.40 (s,br)	2.38 (s)
<b>15</b>	2.68 (d) <sup>d</sup> $J_{\text{H1a,H2}} = 11.2$	4.39 (dd) $J_{\text{H1s,H2}} = 6.5$ $J_{\text{H1a,H1s}} = 1.1$	5.02 (app dt) $J_{\text{H1s,H2}} = 6.6$ $J_{\text{H1a,H2}} = 11.0$ $J_{\text{H2,H3}} = 9.7$	2.07 (t) <sup>c</sup> $J_{\text{H2,H3(H4)}} = 9.5$	8.63 (d) $J_{\text{H3,H4}} = 9.5$	2.10 (s)
<b>16'</b>	2.21 (dt) $J_{\text{H1a,H2}} = 11.3$ $^4J = 0.9$	4.03 (d) $J_{\text{H1s,H2}} = 7.0$	4.80 (ddd) $J_{\text{H1a,H2}} = 11.3$ $J_{\text{H2,H3}} = 10.0$ $J_{\text{H1s,H2}} = 7.0$	2.57 (ddt) $J_{\text{H2,H3}} = 9.9$ $J_{\text{H3,H4}} = 5.9$ $^4J = 0.7$	9.54 (d) $J_{\text{H3,H4}} = 5.9$	2.14 (s)
	2.20 (d,br) <sup>d</sup> $J_{\text{H1a,H2}} = 11.4$	4.01 (d) $J_{\text{H1s,H2}} = 6.9$	4.70 (ddd) $J_{\text{H1a,H2}} = 11.3$ $J_{\text{H2,H3}} = 9.9$ $J_{\text{H1s,H2}} = 7.0$	2.50 <sup>c</sup>	9.38 (d) $J_{\text{H3,H4}} = 7.2$	2.13 (s)
<b>17<sup>e</sup></b>	2.40 (d, br) $J_{\text{H1a,H2}} = 11.4$	3.64 (d) $J_{\text{H1s,H2}} = 7.1$	4.68 (dt) $J_{\text{H1s,H2}} = 7.1$ $J_{\text{H2,H3}} = 10.1$ $J_{\text{H1a,H2}} = 11.3$	2.81 (dd) $J_{\text{H3,H4}} = 5.7$ $J_{\text{H2,H3}} = 10.0$	9.45 (d) $J_{\text{H3,H4}} = 5.7$	2.24 (s)
	2.36 (dt) <sup>d</sup> $J_{\text{H1a,H2}} = 11.4$ $^4J = 1.0$	3.56 (d) $J_{\text{H1s,H2}} = 7.2$	4.52 (ddd) $J_{\text{H1s,H2}} = 7.1$ $J_{\text{H2,H3}} = 10.0$ $J_{\text{H1a,H2}} = 11.4$	2.72 (dd) $J_{\text{H3,H4}} = 6.1$ $J_{\text{H2,H3}} = 10.0$	9.33 (d) $J_{\text{H3,H4}} = 6.2$	2.20 (s)
<b>18<sup>f</sup></b>	2.37 (d) $J_{\text{H1a,H2}} = 11.3$	3.65 (d) $J_{\text{H1s,H2}} = 7.0$	4.69 (ddd) $J_{\text{H1s,H2}} = 7.0$ $J_{\text{H2,H3}} = 10.0$ $J_{\text{H1a,H2}} = 11.5$	2.79 (dd) $J_{\text{H3,H4}} = 5.8$ $J_{\text{H2,H3}} = 10.0$	9.45 (d) $J_{\text{H3,H4}} = 5.7$	2.24 (s)
<b>19-endo</b>	1.59 (d) <sup>d</sup> $J_{\text{H1a,H2}} = 11.4$	3.71 (d,br) $J_{\text{H1s,H2}} = 6.7$	4.71 (tt) $J_{\text{H1s,H2}} = 6.9$ $J_{\text{H1a,H2}} = 11.4$			2.42 (s)
<b>19-exo</b>	2.20 (app dt) <sup>d</sup> $J_{\text{H1a,H2}} = 11.4$ $J_{\text{H1a,H1s}} = 1.2$	3.03 (app dt) $J_{\text{H1s,H2}} = 6.7$ $J_{\text{H1a,H1s}} = 1.2$	3.81 (tt) $J_{\text{H1s,H2}} = 6.9$ $J_{\text{H1a,H2}} = 11.4$			2.45
<b>20</b>	2.51 (dd) $J_{\text{H1a,H2}} = 11.3$ $^4J = 0.8$	3.43 (d) $J_{\text{H1s,H2}} = 7.1$	4.53 (ddd) $J_{\text{H1a,H2}} = 11.3$ $J_{\text{H2,H3}} = 9.9$ $J_{\text{H1s,H2}} = 7.1$	3.08 (dd) $J_{\text{H2,H3}} = 9.9$ $J_{\text{H3,H4}} = 5.6$	9.39 (d) $J_{\text{H3,H4}} = 5.6$	2.05 (s)
	3.00 (dd) <sup>c</sup> $J_{\text{H1a,H2}} = 11.4$ $^4J = 0.7$	3.13 (d) $J_{\text{H1s,H2}} = 7.0$	4.32 (ddd) $J_{\text{H1a,H2}} = 11.4$ $J_{\text{H2,H3}} = 10.0$ $J_{\text{H1s,H2}} = 7.0$	3.71 (dd) $J_{\text{H2,H3}} = 10.0$ $J_{\text{H3,H4}} = 3.1$	9.66 (d) $J_{\text{H3,H4}} = 3.1$	1.57 (s)

<sup>a</sup> For numbering see corresponding schemes. (CD<sub>3</sub>)<sub>2</sub>CO,  $\delta$ ,  $J$  = coupling constant in Hz; (s) singlet; (d) doublet; (t) triplet; (q) quartet; (m) multiplet; (br) broad; (app) apparent. <sup>b</sup>Overlapped signal. <sup>c</sup>In C<sub>6</sub>D<sub>6</sub>. <sup>d</sup>In CD<sub>3</sub>NO<sub>2</sub>. <sup>e</sup>MeCN, **17**: 2.62 (s); 2.46 (s)<sup>d</sup>. <sup>f</sup>EtCN, **18**: 2.97 (q, CH<sub>2</sub>, 7.5), 1.33 (t, Me, 7.5).

MeOH (9:1) provides two fractions. The first fraction consists of one brown and one yellow band. A second column, eluted with the same solvent mixture, resolves both components. After discarding the initial brown band, the oxopentadienyl product **9** is isolated from the first yellow fraction as a yellow powder in 38% yield (Figure 3). The second fraction affords a yellow

band, which consists of a dinuclear hexamethylbenzene ruthenium compound, which remains under investigation.

Alternatively, the crude reaction mixture can be triturated with CH<sub>2</sub>Cl<sub>2</sub> or acetone/diethyl ether to afford an oily dark yellow solid consisting of a mixture of mesityl oxide and complex **9**, the former produced by adventitious hydrolysis or, possibly,

Table 4.  $^{13}\text{C}$  NMR Data<sup>a</sup> for Compounds 9–11 and 13–20

compound	C1	C2	C3	C4	C5	C6	C <sub>6</sub> Me <sub>6</sub>	C <sub>6</sub> Me <sub>6</sub>
<b>9</b>	63.94	112.87	82.83	156.37	22.74	22.57	102.50	16.48
<b>10</b>	51.74	101.84	84.14	87.28	43.59	23.84	103.88	16.24
<b>11</b>	56.52	106.62	62.68	205.11	18.85	31.15	98.05	15.17
	56.71 <sup>b</sup>	106.32	62.97	204.88	18.84	31.31	96.96	14.85
<b>13</b>	58.52 <sup>b</sup>	107.43	68.10	205.61	31.29	19.69	87.86 (C <sub>6</sub> H <sub>6</sub> )	
<b>14</b>	67.38	99.00	89.25	138.42			104.33	16.84
	66.73 <sup>c</sup>	97.84	88.12	136.85			103.59	15.69
<b>15</b>	65.48 <sup>c</sup>	95.32	75.68	203.18			100.97	15.26
<b>16'</b>	59.74	94.23	70.50	200.52			99.24	15.72
<b>17<sup>d</sup></b>	54.70	91.10	65.95	198.55			101.66	16.05
	53.77 <sup>c</sup>	90.49	65.04	198.59			100.94	14.94
<b>18<sup>e</sup></b>	54.81	91.07	66.05	198.54			101.68	16.04
<b>19-endo</b>	49.94	96.00		n.o.			111.97	16.42
<b>19-exo</b>	44.55	86.34		197.40			110.16	15.84
<b>20</b>	56.20	90.88	67.89	199.02			98.58	15.72
	56.22 <sup>c</sup>	88.04	66.72	197.77			97.44	15.11

<sup>a</sup> For numbering see corresponding schemes. (CD<sub>3</sub>)<sub>2</sub>CO,  $\delta$ . <sup>b</sup>In C<sub>6</sub>D<sub>6</sub>. <sup>c</sup>In CD<sub>3</sub>NO<sub>2</sub>. <sup>d</sup>MeCN, **17**: 4.09 (Me), 128.92 (C); 2.27 (Me)<sup>c</sup>, 127.60 (C)<sup>c</sup>. <sup>e</sup>EtCN, **18**: 10.45 (Me), 13.39 (CH<sub>2</sub>), 132.48 (C).

condensation of the coordinated acetone.<sup>12,22</sup> This mixture can be purified by repeated recrystallization, providing oxopentadienyl complex **9** as yellow crystals in a significantly improved 58% yield. After purification of compound **9**, NMR spectroscopic analysis of the crystalline material (Tables 3 and 4) in acetone-*d*<sub>6</sub> shows two sets of resonances in a ratio of approximately 5:1, consisting of complex **9** and a small amount of the enol tautomer, [( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)Ru(2-hydroxy-4-methyl- $\eta^5$ -pentadienyl)]BF<sub>4</sub> (**10**). In the <sup>1</sup>H NMR spectrum, downfield resonances are observed at  $\delta$  5.89 and 5.65 for the central (H3) protons of **9** and **10**, respectively. Both signals for the *syn* (H1:  $\delta$  2.88, H5:  $\delta$  2.65) and *anti* (H1:  $\delta$  0.81, H5:  $\delta$  0.93) protons of pentadienyl isomer **10** appear significantly upfield from the corresponding signals of oxopentadienyl complex **9** (H<sub>1syn</sub>:  $\delta$  3.95, H<sub>1anti</sub>:  $\delta$  2.29), which may reflect the greater back-donation from the metal in complex **10**. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, three upfield signals ( $\delta$  43.59, 51.74, and 63.94) can be assigned to the terminal methylene groups of the two tautomers. Quaternary peaks appear at  $\delta$  156.37 (**9**) and 87.28 (**10**), characteristic of the -(Me)C=O and -(OH)C=CH<sub>2</sub> residues, respectively. The <sup>1</sup>H NMR chemical shifts of the oxopentadienyl ligand in complex **9** are similar to those observed for their cationic congeners, [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)M(2,4-dimethyl- $\eta^5$ -oxopentadienyl)] (M = Rh<sup>+</sup>, Ir<sup>+</sup>).<sup>22,23</sup> As expected, oxopentadienyl carbon and hydrogen resonances of **9** are shifted to higher frequencies compared to the neutral [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ru(2,4-dimethyl- $\eta^5$ -oxopentadienyl)],<sup>1b,3a</sup> consistent with the change in overall charge from neutral to cationic. The spectroscopy of complex **10** bears close similarity to that of the isoelectronic iridium complex<sup>22</sup> [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ir(2-hydroxy-4-methyl- $\eta^5$ -pentadienyl)]<sup>+</sup>, as well as to complexes **2–4**.

The origin of the minor enol tautomer **10** remains obscure; several control experiments demonstrate that there is no straightforward equilibrium isomerization from **9** to **10**, as it has been proposed in the isoelectronic iridium system [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ir(2,4-dimethyl- $\eta^5$ -oxopentadienyl)]<sup>+</sup> and [( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)Ir(2-hydroxy-4-methyl- $\eta^5$ -pentadienyl)]<sup>+</sup>, both derived from the analogous reaction of dicationic complex [Cp<sup>\*</sup>Ir(acetone)<sub>3</sub>]<sup>2+</sup>.<sup>22</sup> Thermolysis of the pure oxopentadienyl complex **9**, either in acetone at 50 °C for several days or in acetonitrile at 100 °C for 20 h, showed no conversion to the corresponding pentadienyl tautomer **10**. Thermolysis of the mixture of **9** and **10** for 20 h

at 100–110 °C does not show any interconversion, although the formation of minor unidentified products is noted. Further, no isomerization is observed upon the addition of catalytic HBF<sub>4</sub> to a solution of complex **9** in acetone-*d*<sub>6</sub>, even upon heating for several days. Prolonged heating of **1** in acetone shows no evidence for the formation of either complex **9** or **10**.

No further improvement in either the conversion or the yield of oxopentadienyl complex **9** was observed by starting from either the corresponding tris(acetonitrile) solvate, [( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)Ru(NCMe)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub>, or the considerably less stable tetrahydrofuran analogue, [( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)Ru(THF)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub>. The former reaction with 1,3-dimethyl-1-trimethylsilyloxy-1,3-butadiene proceeds at reflux (7 h) to give an inseparable mixture of starting material and complex **9** in an approximately 1:1 ratio. In the latter reaction, the orange, highly labile [( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)Ru(THF)<sub>3</sub>]<sup>2+</sup> intermediate is sparingly soluble in THF and affords only traces of complex **9**, presumably as a function of the poor solubility. The <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) spectrum of the tentatively identified [( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)Ru(THF)<sub>3</sub>]<sup>2+</sup> shows consistent arene and coordinated THF resonances at  $\delta$  2.36 (s, C<sub>6</sub>Me<sub>6</sub>), 3.41 (m, CH<sub>2</sub>), and 1.61 (m, CH<sub>2</sub>).

Oxopentadienyl complex **9** is obtained cleanly from the reaction of [( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)Ru(2,4-dimethyl- $\eta^3$ -*exo-syn*-oxopentadienyl)Cl] (**11**) with silver tetrafluoroborate in acetone (Scheme 2). Unfortunately, the latter material is obtained in very poor yield from the alkylation of [( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)RuCl<sub>2</sub>]<sub>2</sub> with the corresponding lithium oxopentadienide in THF at room temperature (15–19% isolated yield). All attempts to improve this alkylation by inclusion of *N,N'*-dimethylpropyleneurea (DMPU) as a cosolvent or through the use of alternative precursors such as [( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)Ru(pyridine)Cl<sub>2</sub>] (**12**)<sup>24</sup> were unsuccessful.<sup>25</sup>

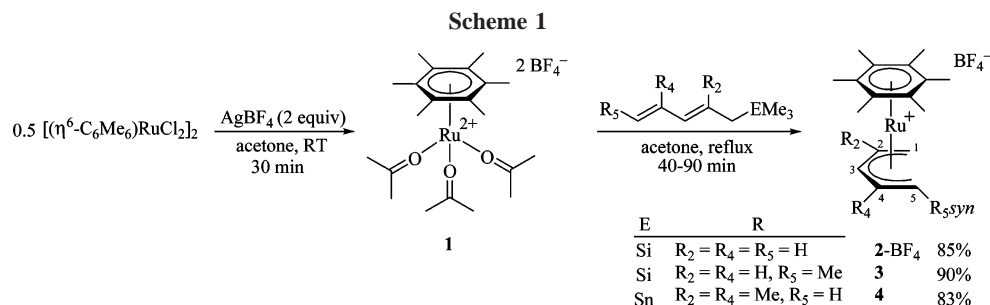
The corresponding parent complex, [( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)Ru(2,4-dimethyl- $\eta^3$ -*exo-syn*-oxopentadienyl)Cl] (**13**), can be prepared from the reaction of the lithium oxopentadienide with the corresponding dimer [( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)RuCl<sub>2</sub>]<sub>2</sub>, but the reaction does not go to completion and also produces several unidentified byproducts, which complicate the isolation of pure oxopentadienyl products. <sup>1</sup>H NMR spectroscopy allows the assignment of complex **13**, as well as the tentative isomeric congener **13-endo** (Table 3).

(24) Steedman, A. J.; Burrell, A. K. *Acta Crystallogr., Sect. C* **1997**, 53, 864–866.

(25) The reaction of lithium oxopentadienide with [( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)RuCl<sub>2</sub>]<sub>2</sub> in a mixture of THF and DMPU (4:1) affords compound **11** in approximately 15% yield; similar results were obtained from the reaction of lithium oxopentadienide with [( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)Ru(pyridine)Cl<sub>2</sub>] (see Experimental Section).

(22) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Organomet. Chem.* **1977**, 134, 319–325.

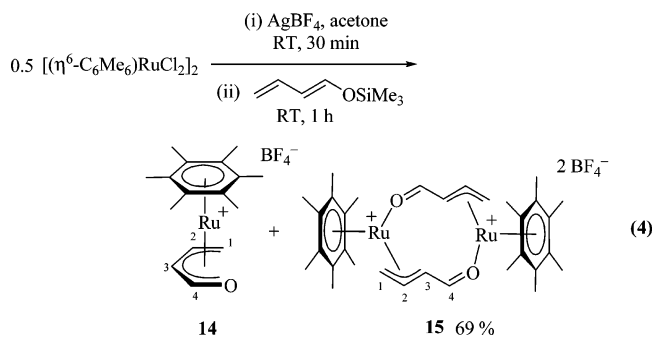
(23) Rangel-Salas, I. I.; Paz-Sandoval, M. A.; Nöth, H. *Organometallics* **2002**, 21, 4696–4710.



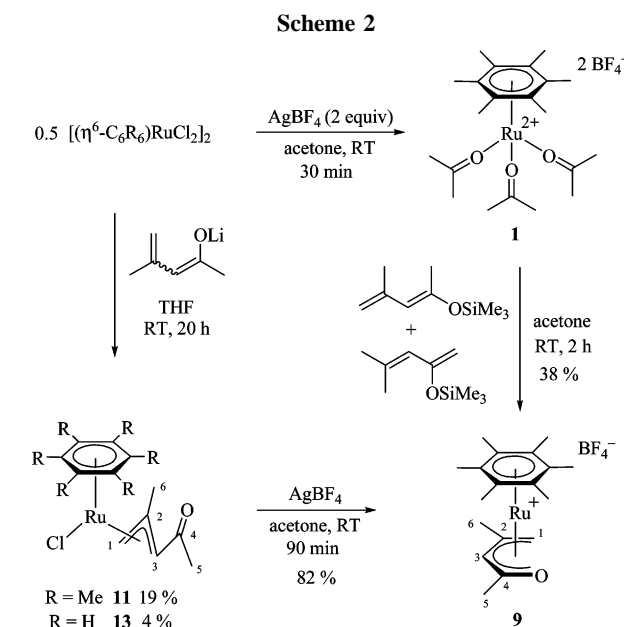
The yield of complex **13** is vanishingly low (4%), as might be anticipated for an  $\eta^6$ -benzene derivative, which is considerably less stable than the hexamethylbenzene analogue. Although complex **13** is reasonably stable in the solid state, both **13** and **13-endo** are unstable in solution.

Infrared and NMR spectroscopy (Tables 3 and 4) reveal that the oxopentadienyl ligands in complexes **11** and **13** adopt an  $\eta^3$ -oxodienyl coordination mode, retaining an inner sphere chloride ligand. The thermodynamically preferred *exo-syn* configuration is assigned to this ligand in complex **11**, as determined by NOE difference experiments. Similar trends in chemical shifts are observed in the analogous complexes  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(2,4\text{-dimethyl-}\eta^3\text{-exo-oxodienyl})\text{Cl}_2]^{20}$  and  $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(2,4\text{-dimethyl-}\eta^3\text{-exo-oxodienyl})\text{Cl}]$  ( $\text{M} = \text{Rh, Ir}$ ).<sup>23</sup> In the  $^{13}\text{C}$  NMR spectra of both complexes **11** and **13**, the carbonyl resonances (C4) appear strongly deshielded at  $\delta$  204.88 and 205.61, while the  $\nu_{\text{CO}}$  absorptions in the infrared spectra are observed at 1656 and 1659  $\text{cm}^{-1}$ , respectively. X-ray diffraction analyses of both complexes **11** and **13** confirm the *exo-syn* configurations in the solid state (Figures 4 and 5). The *endo* structure assigned to the minor isomer of complex **13** is suggested by the strong similarity in  $^1\text{H}$  NMR chemical shifts [ $\text{C}_6\text{D}_6$ :  $\delta$  4.81 (s, 1H), 4.57 (s, 6H), 4.04 (d, 1H), 3.47 (s, 1H), 2.19 (s, 3H), 1.01 (s, 3H)] to those observed for the known *endo* isomers of  $[\text{Cp}^*\text{Ru}(\eta^3\text{-oxodienyl})\text{Cl}_2]$ .<sup>3a,20</sup>

For synthetic purposes, access was desired to less substituted oxopentadienyl complexes, including the completely unsubstituted system. The reaction of **1** with 1-trimethylsilyloxy-1,3-butadiene, however, provided an unexpected contrast. After the addition, an orange precipitate and yellow solution are obtained. After filtration and concentration of the solution, a dark yellow, oily solid is isolated, spectroscopically characterized as the  $\eta^5$ -oxopentadienyl complex  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-oxopentadienyl})]\text{-BF}_4$  (**14**) (eq 4). Unfortunately, this product is accompanied by several minor impurities, which could not be separated. The orange precipitate, tentatively assigned as the dimeric  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\mu_2\text{-1-3,5-}\eta\text{-exo-syn-oxopentadienyl})_2(\text{BF}_4)_2]$  (**15**) on the basis of its chemical reactivity, was isolated in 69% yield. The coordination sphere and dimeric structure was confirmed in the solid state by X-ray crystallography (Figure 6).



Addition of water to an acetone suspension of dimeric **15** affords the monomeric aquo adduct  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-exo-syn-oxodienyl})(\text{H}_2\text{O})]\text{BF}_4$  (**16**), but this complex is unstable toward



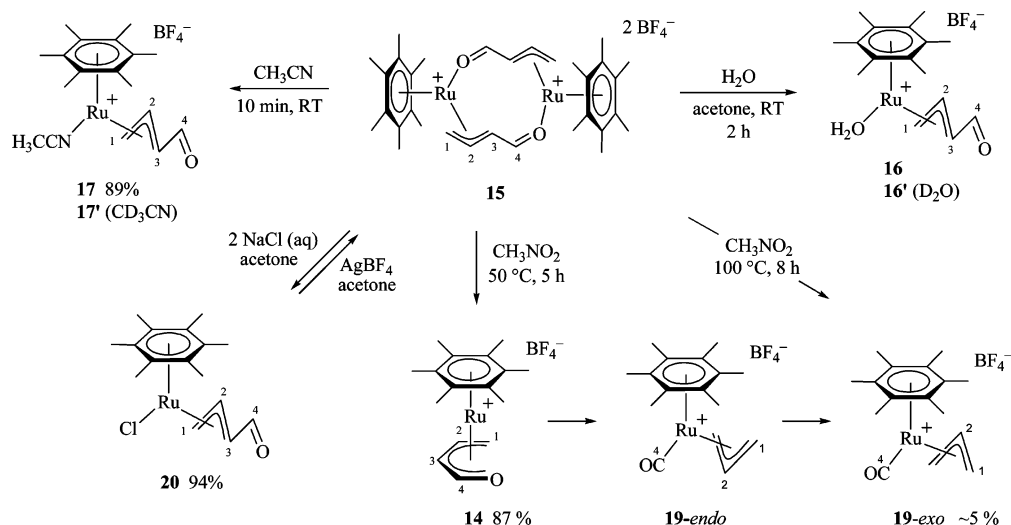
isolation, reverting back to the dimer upon precipitation or slow crystallization from acetone/diethyl ether (Scheme 3). A more stable adduct,  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-exo-syn-oxodienyl})(\text{MeCN})]\text{-BF}_4$  (**17**), is formed upon dissolution in acetonitrile at room temperature, isolated as a yellow microcrystalline powder in 89% yield by crystallization from acetonitrile/diethyl ether (Scheme 3). Addition of  $\text{D}_2\text{O}$  to a suspension of **15** in acetone- $d_6$  affords a yellow solution of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-exo-syn-oxodienyl})(\text{D}_2\text{O})]\text{BF}_4$  (**16'**) quantitatively, although the same reaction in nitromethane- $d_3$  affords a mixture of **15** and **16'** in an invariant 1:6.5 ratio, respectively. Addition of  $\text{CD}_3\text{CN}$  to each reaction mixture affords  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-exo-syn-oxodienyl})(\text{CD}_3\text{CN})]\text{BF}_4$  (**17'**) exclusively, corroborated by comparison with the  $^1\text{H}$  NMR spectrum of pure isolated **17**.

In nitromethane- $d_3$ , the dimeric  $\eta^3$ -coordinated complex **15** transforms quantitatively to  $\eta^5$ -oxopentadienyl complex **14** upon standing for one week at room temperature or upon heating to 50  $^\circ\text{C}$  for 5 h. On a preparative scale using reagent grade nitromethane, the propionitrile adduct  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-exo-syn-oxopentadienyl})(\text{EtCN})]\text{BF}_4$  (**18**) is unexpectedly obtained. Spectroscopic identification of the propionitrile impurity in nitromethane (Aldrich) clearly establishes the origin of this product. Complex **14** is obtained after 5 h at 50  $^\circ\text{C}$  provided the reaction is conducted in high-purity nitromethane (99+%).

Upon heating to higher temperature, complex **14** undergoes decarbonylation (Scheme 3), producing  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-endo-C}_3\text{H}_5)(\text{CO})]\text{BF}_4$  (**19-endo**) kinetically, followed by slower isomerization to the thermodynamic *exo* isomer,  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-exo-C}_3\text{H}_5)(\text{CO})]\text{BF}_4$  (**19-exo**) (Figure 7). This reaction, presumably proceeding via initial hapticity change(s) and subsequent carbon-hydrogen and carbon-carbon bond activa-



Scheme 3



tion, is consistent with the formation of  $\text{Cp}^*\text{Ru}(\text{allyl})(\text{CO})$  observed upon attempted synthesis of unsubstituted  $\eta^5$ -oxopentadienyl complexes in the pentamethylcyclopentadienyl series.<sup>26</sup>

The formation of  $\eta^5$ -coordinated complex **14** from the *exo-syn*-substituted  $\eta^3$ -allyl precursor **15** presumably arises from some combination of  $\eta^3$ -allyl/ $\eta^1$ -allyl,  $\eta^3$ -allyl/ $\eta^3$ -oxoallyl, and  $\eta^3$ -oxoallyl/ $\eta^1$ -oxoallyl equilibria accompanied by single bond rotations. Such pathways should be accelerated by the use of weakly coordinating solvents, as observed. Given the dimeric nature of complex **15**, this reorganization could also be assisted by dissociation of the bridging ketone ligands accompanied by transient metal–metal bond formation, exploiting the presence of the adjacent metal centers. While  $\eta^3$ -oxoallyl coordination is unprecedented in ruthenium chemistry, very similar isomerizations have been observed in related rhodium complexes, e.g.,  $(\text{PPh}_3)_2\text{Rh}(\eta^3\text{-CH}_2\text{C}(\text{Ph})\text{O})$ .<sup>27</sup>

Finally, the addition of aqueous  $\text{NaCl}$  to a suspension of dimeric complex **15** in acetone at room temperature affords neutral  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-exo-syn-oxodienyl})\text{Cl}]$  (**20**) (Scheme 3). This complex is closely analogous to  $\eta^3$ -oxodienyl complex

**11** (Scheme 2), but in contrast to the latter, treatment with silver tetrafluoroborate leads not to an  $\eta^5$ -oxopentadienyl complex but instead to dimer **15** as the major product, accompanied by unreacted **20** and traces of unidentified byproducts.

Comparative NMR spectroscopic data for complexes **14**–**20** are summarized in Tables 3 and 4. The pronounced high-frequency chemical shift of H4 observed for the  $\eta^3$ -coordinated dimer **15** as compared to  $\eta^5$ -coordinated **14** reflects the greater influence of the metal coordination, as typically observed for  $\eta^5$ -oxopentadienyl coordination. Both H3 and H4 resonances show chemical shifts consistent with those observed for neutral analogues  $[\text{Cp}^*\text{Ru}(\eta^3\text{-oxodienyl})\text{Cl}_2]$  and  $[\text{Cp}^*\text{Ru}(\eta^5\text{-oxopentadienyl})]$ .<sup>3b</sup> The  $^{13}\text{C}$  NMR chemical shifts for C4 (**14**:  $\delta$  136.85, **15**: 203.18) clearly reflect the different bonding modes for the two complexes. The *exo-syn* configuration of the  $\eta^3$ -allyl ligands in oxopentadienyl complexes **16**–**18** and **20** has been confirmed by NOE difference measurements, which show strong interactions between the terminal hydrogen atoms, H1 and H3, as well as between adjacent hydrogen atoms H3 and H4 in each of these ligands. The decarbonylated complexes

Table 5. X-ray Data Collection Parameters for Compounds **2-BF<sub>4</sub>**, **4**, **9**, **11**, **13**, **15**, and **19-exo**

	<b>2-BF<sub>4</sub></b>	<b>4</b>	<b>9</b>	<b>11</b>	<b>13</b>	<b>15</b>	<b>19-exo</b>
formula	$\text{C}_{17}\text{H}_{25}\text{BF}_4\text{Ru}$	$\text{C}_{19}\text{H}_{29}\text{BF}_4\text{Ru}$	$\text{C}_{18}\text{H}_{27}\text{BF}_4\text{ORu}$	$\text{C}_{18}\text{H}_{27}\text{ClORu}$	$\text{C}_{12}\text{H}_{15}\text{ClORu}$	$\text{C}_{16}\text{H}_{23}\text{BF}_4\text{ORu}$	$\text{C}_{16}\text{H}_{23}\text{BF}_4\text{ORu}$
fw	417.25	445.31	447.28	395.92	311.76	419.22	419.22
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>Pbcm</i> (No. 57)	<i>P2<sub>1</sub>/m</i> (No. 11)	<i>P2<sub>1</sub>/c</i> (No. 14)	<i>C2/c</i> (No. 15)	<i>Cc</i> (No. 9)	<i>P2<sub>1</sub>/n</i> (No. 14)	<i>P2<sub>1</sub>/c</i> (No. 14)
<i>a</i> (Å)	7.1986 (6)	7.2395(3)	7.3015 (10)	15.1854 (8)	6.9706 (6)	10.1685(2)	12.5954(3)
<i>b</i> (Å)	15.8569 (13)	13.2414(7)	16.357 (2)	8.8972 (5)	23.078 (2)	7.9340(2)	9.4753(2)
<i>c</i> (Å)	15.3300 (13)	10.0674(5)	31.109 (4)	25.5390 (14)	7.7517 (7)	21.2941(5)	15.5362(4)
$\alpha$ (deg)	90	90	90	90	90	90	90
$\beta$ (deg)	90	95.796(2)	92.279 (3)	93.4100 (10)	110.2905 (11)	102.3080(1)	111.934(1)
$\gamma$ (deg)	90	90	90	90	90	90	90
<i>V</i> (Å <sup>3</sup> )	1749.9 (3)	960.14(8)	3712.4 (8)	3444.4 (3)	1169.60 (18)	1678.46(7)	1719.96(7)
<i>Z</i>	4	2	8	8	4	4	4
cryst size (mm)	0.30 × 0.28 × 0.10	0.15 × 0.15 × 0.15	0.49 × 0.20 × 0.04	0.19 × 0.18 × 0.15	0.52 × 0.37 × 0.23	0.20 × 0.075 × 0.05	0.40 × 0.40 × 0.15
<i>D</i> <sub>calc</sub> (g cm <sup>−3</sup> )	1.584	1.540	1.601	1.527	1.770	1.659	1.619
temp (K)	193	293	193	193	193	293	293
diffractometer	Bruker PLATFORM/SMART 1000 CCD	Enraf-Nonius Kappa CCD	Bruker PLATFORM/SMART 1000 CCD	Bruker PLATFORM/SMART 1000 CCD	Bruker PLATFORM/SMART 1000 CCD	Enraf-Nonius Kappa CCD	Enraf-Nonius Kappa CCD
2 $\theta$ scan range (deg)	5.14 to 51.58	4.0 to 57.4	4.65 to 51.55	5.30 to 52.76	5.60 to 52.78	7.10 to 54.94	6.78 to 57.34
index ranges	−8 ≤ <i>h</i> ≤ 8 −19 ≤ <i>k</i> ≤ 19 −19 ≤ <i>l</i> ≤ 19	−9 ≤ <i>h</i> ≤ 8 −17 ≤ <i>k</i> ≤ 16 −10 ≤ <i>l</i> ≤ 13	−8 ≤ <i>h</i> ≤ 8 −19 ≤ <i>k</i> ≤ 19 −36 ≤ <i>l</i> ≤ 36	−18 ≤ <i>h</i> ≤ 18 −11 ≤ <i>k</i> ≤ 10 −37 ≤ <i>l</i> ≤ 31	−8 ≤ <i>h</i> ≤ 8 −28 ≤ <i>k</i> ≤ 28 −9 ≤ <i>l</i> ≤ 9	−12 ≤ <i>h</i> ≤ 13 −10 ≤ <i>k</i> ≤ 9 −9 ≤ <i>l</i> ≤ 27	−16 ≤ <i>h</i> ≤ 16 −12 ≤ <i>k</i> ≤ 12 −17 ≤ <i>l</i> ≤ 20
no. of reflns collcd	12 821	10 571	32 986	12 079	4209	17 917	24 189
no. of indpt reflns	1851	2560	32 986	3493	2259	3819	4402
no. of indpt obsd	1645 (2 $\sigma$ )	1502 (2 $\sigma$ )	25865 (2 $\sigma$ )	3125 (2 $\sigma$ )	2240 (2 $\sigma$ )	2591 (4 $\sigma$ )	2872 (4 $\sigma$ )
final <i>R</i> <sub>1</sub>	0.0446 (2 $\sigma$ )	0.0486 (2 $\sigma$ )	0.0537 (2 $\sigma$ )	0.0307 (2 $\sigma$ )	0.0159 (2 $\sigma$ )	0.0381 (4 $\sigma$ )	0.0593 (4 $\sigma$ )
final <i>wR</i> <sub>2</sub>	0.1225 (3 $\sigma$ )	0.1006 (2 $\sigma$ )	0.1299 (3 $\sigma$ )	0.0896 (3 $\sigma$ )	0.0410 (3 $\sigma$ )	0.0880 (4 $\sigma$ )	0.1412 (4 $\sigma$ )
GOF	1.075	1.01	1.050	1.117	1.105	1.025	1.035

**Table 6.** Selected Bond Distances (Å) of Compounds **2-BF<sub>4</sub>**, **4**, **9**, **11**, **13**, **15**, and **19-*exo***

	<b>2-BF<sub>4</sub></b>	<b>4</b>	<b>9</b>	<b>11</b>	<b>13</b>	<b>15</b>	<b>19-<i>exo</i></b>
C4–O1			1.314(4) A 1.309(4) B	1.218(4)	1.221(3)	1.257(4)	1.126(6)
C1–C2	1.530(16)	1.422(9)	1.381(5) A 1.410(5) B	1.434(6)	1.417(4)	1.374(6)	1.420(9)
C2–C3	1.448(17)	1.409(7)	1.436(5) A 1.421(5) B	1.411(5)	1.438(4)	1.441(5)	1.389(9)
C3–C4	1.447(13)		1.441(5) A 1.413(5) B	1.467(5)	1.478(4)	1.416(5)	
C4–C5	1.364(16)		1.476(5) A 1.495(5) B	1.504(6)	1.505(4)		
C2–C6		1.521(11)	1.500(4) A 1.495(5) B	1.513(5)	1.510(5)		
C11–C12	1.415(6)		1.434(5) A 1.450(5) B	1.405(4)	1.413(4)	1.418(5)	1.401 (9)
C12–C13	1.421(7)		1.397(5) A 1.391(5) B	1.435(4)	1.394(4)	1.429(5)	1.393 (9)
C13–C14			1.433(5) A 1.435(5) B	1.425(4)	1.436(6)	1.423(5)	1.452(11)
C14–C15			1.402(5) A 1.415(5) B	1.435(4)	1.39.1(4)	1.442(6)	1.419(11)
C15–C16			1.445(5) A 1.429(5) B	1.410(4)	1.415(4)	1.407(6)	1.413(8)
C11–C16			1.418(5) A 1.408(5) B	1.447(4)	1.416(5)	1.441(6)	1.385(8)
C11–C17	1.508(6)	1.526(11)	1.508(5) A 1.516(5) B	1.511(4)		1.501(6)	1.517(8)
O1–Ru1			2.139(2) A 2.139(2) B			2.153(2)	
C1–Ru1	2.243(12)	2.186(7)	2.168(4) A 2.167(3) B	2.187(3)	2.184(2)	2.204(4)	2.235(5)
C2–Ru1	2.150(11)	2.178(6)	2.206(3) A 2.197 (4) B	2.188(3)	2.174(3)	2.142(4)	2.150(5)
C3–Ru1	2.186(7)	2.197(7)	2.175(3) A 2.206(4) B	2.190(3)	2.180(3)	2.221(3)	2.228(6)
C4–Ru1	2.173(10)		2.202(3) A 2.226(4) B				1.883(6)
C5–Ru1	2.132(12)						
C11–Ru1	2.258(4)	2.249(5)	2.211(3) A 2.214(3) B	2.257(3)	2.158(2)	2.225(4)	2.267(5)
C12–Ru1	2.223(4)	2.235(5)	2.206(4) A 2.223(4) B	2.261(3)	2.244(2)	2.266(4)	2.253(5)
C13–Ru1	2.226(4)	2.272(6)	2.235(4) A 2.274(4) B	2.192(3)	2.231(2)	2.184(3)	2.274(6)
C14–Ru1			2.216(3) A 2.201(3) B	2.234(3)	2.227(3)	2.203(3)	2.292(5)
C15–Ru1			2.202(3) A 2.189(3) B	2.267(3)	2.228(2)	2.298(4)	2.278(5)
C16–Ru1			2.242(4) A 2.234(4) B	2.236(3)	2.175(2)	2.275(4)	2.282(5)
Ru–Cl				2.4258(8)	2.4287(7)		

**19-*endo*** and **19-*exo*** show typical chemical shifts and coupling patterns for  $\eta^3$ -allyl ligands,<sup>28</sup> with deshielded central protons ( $\delta$  4.71–3.81, respectively) and upfield *syn* ( $\delta$  3.71 and 3.03) and *anti* ( $\delta$  1.59 and 2.20) protons. As expected, the central proton of **19-*exo*** is shifted upfield with regard to **19-*endo***, reflecting the internal anisotropy of the coordinated hexamethylbenzene.

**C. Crystallographic Characterization.** The  $\eta^5$ -pentadienyl complex **2-BF<sub>4</sub>** suffers some disorder, but it is unquestionably isostructural with **4**; therefore only **4** is discussed in detail here and a comparison is established with the analogous oxopentadienyl complex **9**. The solid-state structure of  $\eta^3$ -complexes **11**, **13**, **15**, and **19-*exo*** were also determined by X-ray diffraction;

crystallographic data, along with selected bond distances and angles, are given in Tables 5, 6, and 7, respectively. Diagrammatic views of the corresponding molecular structures are provided in Figures 1–7. Figures 1, 2, and 3 clearly reveal the immediate coordination sphere of the coordinatively saturated “half-open sandwich” structures. In the case of oxopentadienyl complex **9**, two crystallographically independent [ $(\eta^6\text{-C}_6\text{Me}_6)\text{-Ru}(\eta^5\text{-2,4-dimethyl-oxopentadienyl})$ ] cations are present in the unit cell. In both oxopentadienyl complexes, the cyclic and acyclic ligands are reasonably planar, with the maximum deviation for the metal-bonded atoms being 0.021(3) and 0.038(3) Å for the hexamethylbenzene ligands and 0.015(2) and 0.011(3) Å for the heteropentadienyl ligands in cations A and B, respectively. Due to the presence of the oxygen atom at the acyclic ligand, the structural parameters of the heterodienyl moiety of **9** were considerably different from those of **4**. The Ru–C bond distances in **4** are quite similar, while for **9** they are not entirely symmetric, Table 6. It is clearly seen in the bond lengths between C1–C2 [1.422(9) Å] and C2–C3 [1.409(7) Å] in compound **4** that there is a full delocalized structure

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Table 7. Selected Bond Angles (deg) of Compounds 2-BF<sub>4</sub>, 4, 9, 11, 13, 15, and 19-*exo*

	2-BF <sub>4</sub>	4	9	11	13	15	19- <i>exo</i>
O1—C4—C3			117.8(3) A 119.2(3) B	125.3(4)	124.6(2)	124.3(3)	174.2(5) <sup>a</sup>
C1—C2—C3	128.0(10)	122.9(6)	120.3(3) A 120.5(3) B	114.3(3)	114.2(3)	116.2(4)	119.4(6)
C2—C3—C4	121.6(7)		126.4(3) A 125.7(3) B	127.3(3)	125.3(3)	126.2(4)	
C1—C2—Ru1	72.9(6)	71.3(4)	70.1(2) A 70.0(2) B	70.8(2)	71.42(16)	74.0(2)	74.4(3)
C2—C3—Ru1	69.1(6)	70.5(4)	72.0(2) A 70.8(2) B	71.13(19)	70.51(16)	67.8(2)	68.5(3)
C3—C2—Ru1	71.8(6)	72.0(4)	69.7(2) A 71.5(2) B	71.26(18)	70.93(17)	73.7(2)	74.6(3)
C4—C3—Ru1	70.1(5)		71.8(2) A 72.2(2) B	116.1(2)	116.72(19)	111.6(2)	
C12—C11—C16			120.6(3) A 119.8(3) B	120.4(3)	120.6(2)	120.4(4)	121.6(5)
C12—C11—Ru1	70.3(2)	71.0(3)	70.9(2) A 71.3(2) B	72.01(18)	74.62(14)	73.2(2)	71.4(3)
C17—C11—Ru1	131.2(3)	128.5(4)	128.3(2) A 128.4(3) B	130.0(2)		126.1(3)	129.1(4)
C11—Ru1—C12	36.82(15)	37.0(2)	37.90(13) A 38.15(14) B	36.23(11)	37.39(10)	36.79(14)	36.1(2)
C1—Ru1—C3	74.4(4)	69.1(2)	68.48(14) A 68.39(13) B	66.19(14)	66.65(13)	65.41(15)	65.8(3)
C1—Ru1—C11	116.5(4)	95.8(2)	119.80(15) A 115.37(14) B	129.36(14)	97.30 (10)	123.69(16)	128.7(2)
C2—Ru1—C11	106.0(3)	124.1(2)	155.08(15) A 150.37(15) B	162.50(14)	95.80(11)	154.73(16)	156.5(2)
C3—Ru1—C13	169.4(2)	111.8(2)	109.62(14) A 111.72(13) B	128.43(11)	161.22(10)	124.45(14)	103.7(2)
C3—Ru1—C16			159.68(14) A 154.60(14) B	125.53(12)	100.50(11)	132.79(14)	154.9(3)
O1—Ru1—C11			100.05(11) A 104.12(12) B			88.51(12)	
O1—Ru1—C16			126.57(11) A 133.13(12) B			92.03(12)	
Cl—Ru1—C1				84.98(11)	85.16(8)		
Cl—Ru1—C2				102.58(10)	104.24(9)		
Cl—Ru1—C3				83.11(9)	85.25(9)		
Cl—Ru1—C14				156.01(9)	91.52(8)		

<sup>a</sup> O1—C4—Ru1.

at the pentadienyl ligand, while the internal oxopentadienyl bonds, for **9**, C2—C3 [1.436(5) Å; 1.421(5) Å]; C3—C4 [1.441(5) Å; 1.413(5) Å], are clearly longer than the external C1—C2 [1.381(5) Å; 1.410(5) Å] or C4—O1 [1.314(4) Å; 1.309(4) Å] ones, pointing to a contribution from a resonance hybrid: short—long—long—short structure in the ligand fragment, charged at the central carbon C3. A similar resonance contribution has been observed in  $[(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(3\text{-methyl-}\eta^5\text{-pentadienyl})]$ .<sup>1b</sup> Both acyclic ligands in **4** and **9** are disposed closer to the metal [2.185(7); 2.178(3) Å, 2.187(4) Å] than is the hexamethylbenzene ligand [2.252(6); 2.219(4) Å, 2.223(4) Å], which may also be caused by the steric effects of the larger ligand. The dihedral angles between the ligand planes for the pentadienyl complex is 11.54°, while for the two crystallographically independent oxopentadienyl structures, the dihedral angles are 8.05(14)° (A) and 7.72(11)° (B). Consistent with other crystallographically characterized half-open sandwich complexes, shorter bonds are observed for the open pentadienyl ligands than for the cyclic ancillary ligands, reflecting the lower  $\pi$ -stabilization of the acyclic fragments as compared to the aromatic ligands (Cp, Cp\*), which have less to gain from additional bonding to the metal.<sup>1b</sup>

A comparison among homoleptic ruthenium sandwich compounds reveals that average Ru—C bond distances increase according to the trend  $\text{Cp}^*_2\text{Ru}$  [2.17(1) Å]<sup>29</sup> < (1,3-dimethyl- $\eta^5$ -cyclopentadienyl)<sub>2</sub>Ru [2.182(5) Å]<sup>30</sup> ~ (2,4-dimethyl- $\eta^5$ -pentadienyl)<sub>2</sub>Ru [2.188(6) Å]<sup>30</sup> < Cp<sub>2</sub>Ru [2.196(3) Å].<sup>31</sup> In

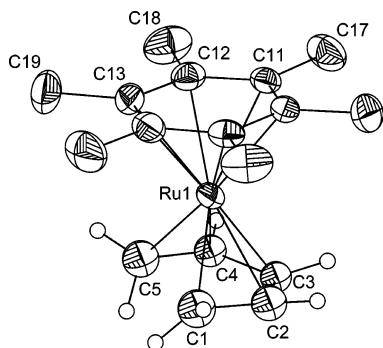
contrast, the heteroleptic half-open ruthenocene complexes show average bond distances for the corresponding cyclic and acyclic ligands of Cp\*Ru(3,5-dimethyl- $\eta^5$ -oxopentadienyl) [2.168(7) and 2.166(7) Å]<sup>1b</sup> ~ Cp\*Ru(2,4-dimethyl- $\eta^5$ -oxopentadienyl) [2.169(7) and 2.168(7) Å]<sup>3a</sup> ~ CpRu(2,4-dimethyl- $\eta^5$ -pentadienyl) [2.179(6) and 2.168(5) Å]<sup>32</sup> < Cp\*Ru(2,4-di-*tert*-butyl- $\eta^5$ -oxopentadienyl) [2.182(8) and 2.193(7) Å]<sup>3a</sup> and Cp\*Ru(2,4-dimethyl- $\eta^5$ -pentadienyl) [2.203(3) and 2.167(3) Å].<sup>1e</sup> This more or less follows the same trend observed for the cationic hexamethylbenzene analogue  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(2,4\text{-dimethyl-}\eta^5\text{-oxopentadienyl})]^+$  (**9**), which shows average bond lengths of 2.219(4), 2.223(4) Å and 2.178(3), 2.187(4) Å for cyclic and acyclic ligands in the two crystallographically independent structures A and B, respectively. For  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(2,4\text{-dimethyl-}\eta^5\text{-pentadienyl})]^+$  (**4**), the corresponding average Ru—C bond values are 2.252(6) and 2.185(7) Å; the average bond distance between the ruthenium and the acyclic ligand thus remains shorter than that observed for the cyclic ligand.

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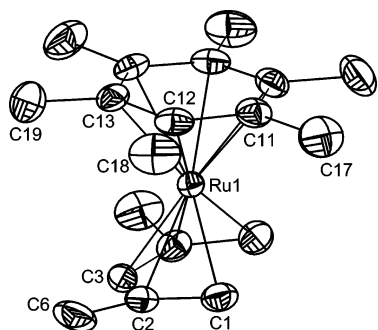
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**Figure 1.** Perspective view of compound **2**-BF<sub>4</sub> drawn at the 30% probability level. Most hydrogen atoms and the BF<sub>4</sub> moiety have been omitted for clarity.

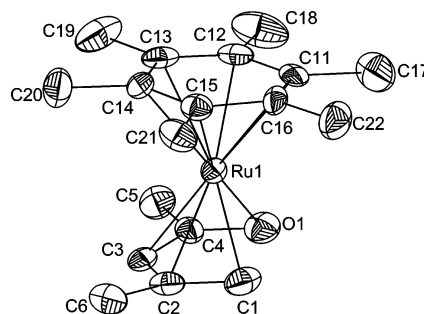


**Figure 2.** Perspective view of compound **4** drawn at the 30% probability level. For purposes of clarity hydrogen atoms and the BF<sub>4</sub> moiety have been omitted.

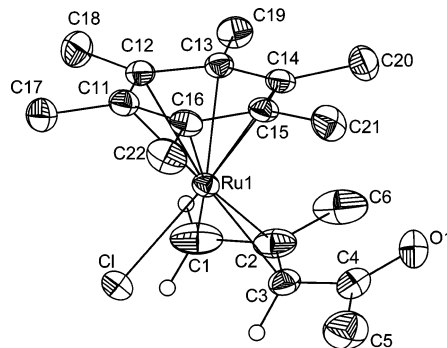
The trend is general: the larger the cyclic ligand, the longer the bond distance to the metal center.

Structural representations of  $\eta^3$ -oxodienyl complexes **11** and **13** are illustrated in Figures 4 and 5, respectively. The  $\eta^3$ -allyl coordination of the oxodienyl ligand is very similar in the two complexes, with respective values for the Ru-oxopentadienyl fragment of C1 [2.187(3), 2.184(2) Å], C2 [2.188(3), 2.174(3) Å], and C3 [2.190(3), 2.180(3) Å]. The noncoordinated fragment of the oxopentadienyl ligand in compound **13** shows a significantly greater distortion from coplanarity with respect to the ancillary ligand [O1–C4–C3–C2 = 18.5(4)°] compared to the corresponding complex **11**, which shows a very slight deviation of 1.3(6)°. Although the metal–arene bond distances C11–C16 reflect the expectedly higher steric demand of the methyl substituents in the hexamethylbenzene ligand, it is interesting to observe that the values of C11 and C16 in the parent complex **13** are particularly shortened, to 2.158(2) and 2.175(2) Å, as compared with the bond lengths for the remaining carbon atoms, which average 2.233(2) Å. The latter is not significantly different from the average bond distances observed in the hexamethylbenzene complex **11**, which average 2.241(3) Å. The fold angle of 5.08° determined for the C11–C12–C13 and C14–C15–C16 planes of the benzene ring in complex **13** confirms the distortion of the ring away from planarity.

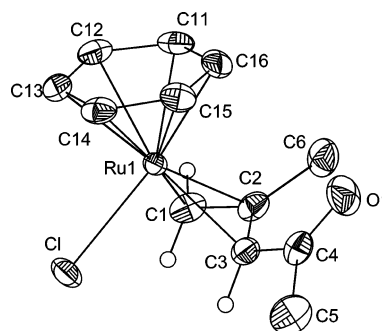
The molecular geometry of dimeric complex **15** is presented in Figure 6. The complex sits on a crystallographic inversion center located at the midpoint of the C3–C4–C3A–C4A rhombus; thus, only half of the molecule is symmetrically independent. Each ruthenium atom is  $\eta^3$ -coordinated to one oxopentadienyl ligand through the C1–C3 allylic fragment and to the symmetry-related oxygen atom of the other oxopentadienyl ligand. Within the allylic fragment, the carbon–carbon bond length of the internal bond [C2–C3: 1.441(5) Å] is clearly



**Figure 3.** Perspective view of compound **9** drawn at the 50% probability level. For purposes of clarity only one crystallographically independent molecule is shown. Hydrogen atoms and the BF<sub>4</sub> moiety have been omitted for clarity.



**Figure 4.** Perspective view of compound **11** drawn at the 50% probability level. Most hydrogen atoms have been omitted for clarity.

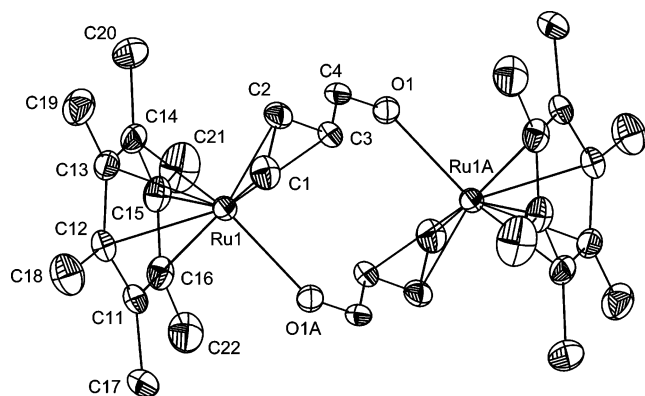


**Figure 5.** Perspective view of compound **13** drawn at the 50% probability level. Most hydrogen atoms have been omitted for clarity.

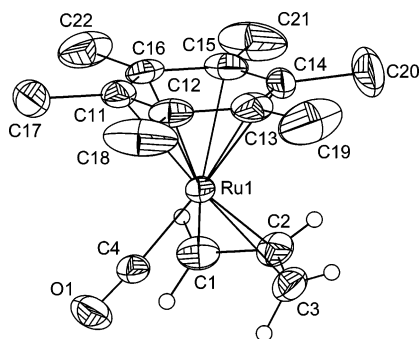
longer than the external bond [C1–C2: 1.374(6) Å], while the C3–C4 single bond and C4–O double bond are particularly short [1.416(5) Å] and long [1.257(4) Å], respectively, suggesting a contribution from resonance delocalization throughout the oxopentadienyl ligand induced by coordination of the carbonyl oxygen to the metal. The structure confirms the *exo-syn* configuration of the oxopentadienyl ligand, analogous to that observed for  $\eta^3$ -coordinated complexes **11** and **13**. The C3–C4–C3A–C4A rhombus is planar and defined by C3–C4–C3A (73.79°) and C4–C3A–C4A (106.21°) angles. To the best of our knowledge, this is the first structurally characterized example of a complex bearing a bridging oxopentadienyl ligand.

The allyl moiety in **19-*exo*** is symmetrically bonded to the metal in an *exo* configuration (Figure 7), with Ru–C terminal distances of 2.235(5) and 2.228(6) Å for Ru1–C1 and Ru1–C3, respectively, while the internal Ru1–C2 is 2.150(5) Å. The C–C bond distances within the allyl ligand are similar [C1–C2 1.420(9); C2–C3 1.389(9) Å]. The C1–C2–C3 angle [119.4(6)°] is quite close to 120°, as typically observed in





**Figure 6.** Perspective view of compound **15** drawn at the 30% probability level. Hydrogen atoms and the  $\text{BF}_4$  moiety have been omitted for clarity.



**Figure 7.** Perspective view of compound **19-*exo*** drawn at the 30% probability level. Most hydrogen atoms and the  $\text{BF}_4$  moiety have been omitted for clarity.

$\eta^3$ -allyl ruthenium structures.<sup>28c,33</sup> The O1–C4–Ru1 angle [174.2(5)°] is bent 6° away from the linearity, while the corresponding angles in the neutral compounds [ $\{\eta^5\text{-C}_6\text{Me}_6(\text{CH}_2\text{CH}=\text{CH}_2)\text{Ru}(\eta^3\text{-*exo*-allyl})(\text{CO})\}$ ]<sup>28c</sup> [176.4(5)°] and [ $\{\eta^5\text{-C}_5\text{H}_5\text{-Ru}(\eta^3\text{-2-methyl-*exo*-allyl})(\text{CO})\}$ ]<sup>33</sup> [179.2(5)°] are closer to 180°. The long bond distance for Ru1–C4 [1.883(6) Å] and the corresponding short bond distance for C4–O1 [1.126(6) Å] reflect the cationic character and deficient back-donation in **19-*exo***, while neutral complexes show, in some sense, better back-donation: [ $\{\eta^5\text{-C}_6\text{Me}_6(\text{CH}_2\text{CH}=\text{CH}_2)\text{Ru}(\eta^3\text{-*exo*-allyl})(\text{CO})\}$ ]<sup>28c</sup> [Ru–C = 1.876(6); C–O = 1.141(6) Å] and [ $\{\eta^5\text{-C}_5\text{H}_5\text{-Ru}(\eta^3\text{-2-methyl-*exo*-allyl})(\text{CO})\}$ ]<sup>33</sup> [Ru–C = 1.841(4); C–O = 1.123(5) Å].

## Experimental Section

**General Procedures.** Standard inert-atmosphere techniques were used for all syntheses and sample manipulations. Solvents were dried by standard methods (hexane and pentane with Na–K/benzophenone or  $\text{CaH}_2$ ; diethyl ether and THF with Na/benzophenone; 1,2-dichloroethane with  $\text{CaH}_2$ ; benzene with Na; ethanol with  $\text{I}_2/\text{Mg}$ ; acetone with  $\text{K}_2\text{CO}_3$  or  $\text{CaSO}_4$ ; and  $\text{CH}_3\text{NO}_2$  with  $\text{CaSO}_4$ ) and distilled under nitrogen prior to use.

Compounds [ $(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2$ ]<sub>2</sub>,<sup>21</sup> 3-bromo-1,5-hexadiene,<sup>34</sup> 1-trimethylsilyl-2,4-pentadiene,<sup>13a</sup> 1-trimethylsilyl-2,4-hexadiene,<sup>13b</sup> 2,4-dimethyl-1-trimethylstannyl-2,4-pentadiene, and 1,3-dimethyl-1-

trimethylsilyloxy-1,3-butadiene isomers<sup>35</sup> were prepared according to literature procedures. All other chemicals, including  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ , 1-trimethylsilyloxy-1,3-butadiene, mesityl oxide, and 1,4-pentadiene were used as obtained from Strem Chemicals, Fluka, or Sigma-Aldrich. Elemental analyses were performed at the University of Alberta and at Cinvestav, using Carlo Erba EA 1108 and Thermo-Finnigan Flash 1112 elemental analyzers, respectively. IR spectra were recorded on a Nic-Plan FTIR microscope attached to a Nicolet Magna 750 FTIR and on Perkin-Elmer 6FPC-FT spectrophotometers in KBr pellets.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on Varian Inova 300 MHz, Varian Inova 400 MHz, Varian Mercury 400 MHz, Jeol GSX-270, Jeol Eclipse-400 MHz, and Bruker Avance DPX 300 MHz spectrometers in dried, deoxygenated, deuterated solvents. NMR chemical shifts are reported relative to residual protium resonance in the solvent.<sup>36</sup> High-resolution mass spectra were obtained using Kratos MS-50 (electron impact ionization, EI), Perspective Biosystems Mariner Biospectrometry Workstation (electrospray ionization, ESI), and Agilent LC/MSD TOF (ESI) spectrometers;  $m/z$  values are given relative to  $^{102}\text{Ru}$ . Melting points were determined using a Gallenkamp apparatus and are not corrected.

**Synthesis of [ $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-CH}_2\text{CHCHCHCH}_2)$ ] $\text{BF}_4$  (**2-BF<sub>4</sub>**).** Into a Schlenk flask equipped with a stir bar were placed [ $\text{Ru}(\eta^6\text{-C}_6\text{Me}_6\text{Cl}_2)_2$ ] (0.30 g, 0.45 mmol) and  $\text{AgBF}_4$  (0.35 g, 1.80 mmol). Acetone (10 mL) was added, and the mixture was stirred for 40 min. The silver chloride precipitate was removed by filtration and rinsed with acetone ( $2 \times 2.5$  mL). The yellow-orange solution thus obtained was transferred to a 50 mL round-bottom flask and 1-trimethylsilyl-2,4-pentadiene (0.19 g, 1.35 mmol) was added. The reaction mixture was heated to reflux for 90 min, and the resultant yellow solution was allowed to warm to room temperature and filtered through Celite. The volatiles were removed *in vacuo*. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$  (~1 mL) and diluted with 5 mL of diethyl ether. The resulting beige precipitate was obtained in 85% yield (0.32 g, 0.77 mmol), after filtration and drying under vacuum. Anal. Calcd for  $\text{C}_{17}\text{H}_{25}\text{BF}_4\text{Ru}$ : C, 48.94; H, 6.04. Found: C, 48.97; H, 6.41. IR (microscope,  $\text{cm}^{-1}$ ): 3012 (w, br), 2928 (w, br), 1447 (m, br), 1391 (s), 1283 (w), 1098 (s), 1051 (vs), 924 (w). HRESI-MS ( $[\text{M} - \text{BF}_4]^+$ ,  $m/z$ ): calcd for  $\text{C}_{17}\text{H}_{25}\text{Ru}$  331.09943; found 331.09919 (error = –0.7 ppm).

**Synthesis of [ $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{\eta^5\text{-CH}_2\text{CHCHCHCH}(\text{Me})\}$ ] $\text{BF}_4$  (**3**).** The reaction was carried out via a procedure similar to that described for **2-BF<sub>4</sub>**, but the silver chloride precipitate was rinsed with acetone ( $2 \times 5$  mL). 1-Trimethylsilyl-2,4-hexadiene (0.28 g, 1.81 mmol) was added, and the mixture was heated to reflux and stirred for 1 h. The resulting beige solid is obtained in 90% yield (0.35 g, 0.81 mmol) as a mixture of [ $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-methyl-}\eta^5\text{-syn-pentadienyl})\text{BF}_4$  (**3-syn**) and [ $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-methyl-}\eta^5\text{-anti-pentadienyl})\text{BF}_4$  (**3-anti**) isomers in a 3:1 ratio, respectively. The *syn* isomer can be separated as yellowish crystals from the crude mixture by fractional crystallization from acetone/diethyl ether (vapor diffusion). A few thin yellowish needles of pure **3-anti** isomer could be selected by manual sorting. Neither **3-syn** nor **3-anti** melts below 350 °C. Anal. Calcd for **3-syn isomer**:  $\text{C}_{18}\text{H}_{27}\text{BF}_4\text{Ru}$ : C, 50.13; H, 6.31. Found: C, 49.97; H, 6.03. IR (microscope,  $\text{cm}^{-1}$ ): 3016 (m, br), 2952 (w, br), 2465 (w, br), 2105 (w, br), 1987 (w, br), 1817 (w, br), 1451 (vs, br), 1391 (vs, br), 1286 (s), 1223 (s), 1031 (vs, br), 958 (vs), 899 (vs), 836 (s), 782 (s), 744 (s). HRESI-MS ( $[\text{M} - \text{BF}_4]^+$ ,  $m/z$ ): calcd for  $\text{C}_{18}\text{H}_{27}\text{Ru}$  345.11507; found 345.11526 (error = 0.5 ppm).

**3-anti isomer:** HRESI-MS ( $[\text{M} - \text{BF}_4]^+$ ,  $m/z$ ) calcd  $\text{C}_{18}\text{H}_{27}\text{Ru}$  345.11507; found 345.11507 (error = 0.0 ppm). IR (microscope,  $\text{cm}^{-1}$ ): 3693 (m), 3652 (m), 3620 (m), 3287 (s, br), 3027 (s), 2919 (vs, br), 2850 (s), 2514 (m, br), 1796 (w), 1731 (m), 1650 (s, br), 1416 (vs, br), 1030 (vs, br), 912 (vs, br), 875 (s), 796 (m).

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**Synthesis of Isomers (2Z,4Z)- and (2E,4Z)-2,4-Dimethyl-1-trimethylstannyl-2,4-pentadiene.** Into a Schlenk flask equipped with a stir bar was placed 5.63 g (50.18 mmol) of potassium *tert*-butoxide. After 8 h under high vacuum, 100 mL of hexane was added. The suspension was placed in a cold bath at  $-78\text{ }^{\circ}\text{C}$ , and 31.4 mL (50.18 mmol) of *n*-BuLi (1.6 M in hexanes) was added. The reaction mixture was allowed to warm to  $0\text{ }^{\circ}\text{C}$ , followed by the addition of 6.47 mL (50.18 mmol) of 2,4-dimethyl-1,3-pentadiene. The resultant yellow solution was stirred overnight. After filtration, the solid residue was rinsed with hexane ( $2 \times 20\text{ mL}$ ), giving 2,4-dimethylpentadienylpotassium in 97% yield (6.5 g, 48.41 mmol) as a pyrophoric cream-colored powder. This was dissolved in 100 mL of THF and cooled to  $-78\text{ }^{\circ}\text{C}$ ; then, trimethyltin chloride (9.66 g, 48.48 mmol) dissolved in hexane was added. The solution changed from yellow to light yellow, and it was slowly warmed to room temperature. The solvent was removed under vacuum, leaving an oily yellow-orange product. Hexane (60 mL) and activated carbon (1 g) were added to the residue and the solution turned colorless. The solution was filtered, and the residue was washed with 60 mL of hexane. After evaporation of the solvent under vacuum, the product was obtained as a colorless oil consisting of a mixture of *Z,Z* and *E,Z* isomers in 2:1 ratio, respectively, in 65% yield (8.09 g, 31.24 mmol).

***Z,Z* isomer:**  $^1\text{H}$  NMR [ $\text{CDCl}_3$ ,  $J(\text{Hz})$ ]  $\delta$  2.05 (s,  $\text{CH}_2$ ,  $J(^1\text{H}-\text{Sn}) = 35.0, 33.9$ ), 1.72 (d, Me,  $J(^1\text{H}-^1\text{H}) = 1.2$ ,  $J(^1\text{H}-\text{Sn}) = 5.8, 7.1$ ), 5.40 (s, br, H-3,  $J(^1\text{H}-\text{Sn}) = 11.4$ ), 1.83 (s, br, Me), 4.86 (s, br, H-5<sub>cis</sub>), 4.68 (s, br, H-5<sub>trans</sub>), 0.13 (s,  $\text{SnMe}_3$ ,  $J(^1\text{H}-\text{Sn}) = 25.2, 26.5$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR [ $\text{CDCl}_3$ ,  $J(\text{Hz})$ ]  $\delta$  20.2 (C-1,  $J(^{13}\text{C}-\text{Sn}) = 143.3, 135.5$ ), 138.6 (C-2), 122.1 (C-3,  $J(^{13}\text{C}-\text{Sn}) = 22.8$ ), 142.8 (C-4), 112.2 (C-5,  $J(^{13}\text{C}-\text{Sn}) = 7.3, 6.3$ ), 27.6 (Me-2,  $J(^{13}\text{C}-\text{Sn}) = 66.4, 73.7$ ), 24.6 (Me-4),  $-9.03$  ( $\text{SnMe}_3$ ,  $J(^{13}\text{C}-\text{Sn}) = 153.6, 160.9$ ).  $^{119}\text{Sn}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.1.

***E,Z* isomer:**  $^1\text{H}$  NMR [ $\text{CDCl}_3$ ,  $J(\text{Hz})$ ]  $\delta$  1.83 (s,  $\text{CH}_2$ ), 1.78 (d, Me,  $J(^1\text{H}-^1\text{H}) = 1.2$ ,  $J(^1\text{H}-\text{Sn}) = 6.1, 7.3$ ), 5.51 (s, br, H-3,  $J(^1\text{H}-\text{Sn}) = 11.4$ ), 1.83 (s, br, Me), 4.86 (s, br, H-5<sub>cis</sub>), 4.69 (s, br, H-5<sub>trans</sub>), 0.11 (s,  $\text{SnMe}_3$ ,  $J(^1\text{H}-\text{Sn}) = 25.2, 26.5$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR [ $\text{CDCl}_3$ ,  $J(\text{Hz})$ ]  $\delta$  26.4 (C-1), 138.6 (C-2), 122.9 (C-3,  $J(^{13}\text{C}-\text{Sn}) = 23.9$ ), 142.7 (C-4), 112.5 (C-5,  $J(^{13}\text{C}-\text{Sn}) = 9.3, 8.3$ ), 20.4 (Me-2), 24.3 (Me-4),  $-9.5$  ( $\text{SnMe}_3$ ,  $J(^{13}\text{C}-\text{Sn}) = 153.5, 160.0$ );  $^{119}\text{Sn}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.0.

**Synthesis of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{CH}_2)]\text{BF}_4$  (4).** The reaction was carried out via a procedure similar to that described for 2-BF<sub>4</sub>, but with  $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)\text{Cl}_2]_2$  (0.20 g, 0.30 mmol), AgBF<sub>4</sub> (0.233 g, 1.20 mmol), and acetone (5 mL). The silver chloride was removed by filtration after stirring 40 min and rinsed with acetone ( $3 \times 5\text{ mL}$ ). The mixture of isomers of 2,4-dimethyl-1-trimethylstannyl-2,4-pentadiene (0.24 g, 0.93 mmol) was added to the filtrate (20 mL), and the reaction was heated to reflux for 40 min with concomitant formation of a black precipitate. After filtration through Celite, evaporation of the yellow solution afforded 0.22 g (0.49 mmol, 83%) of a microcrystalline yellow solid. Yellowish single crystals were obtained by slow evaporation of an acetone solution at room temperature. The crystals do not melt below  $350\text{ }^{\circ}\text{C}$ . Anal. Calcd for  $\text{C}_{19}\text{H}_{29}\text{BF}_4\text{Ru}$ : C, 51.25; H, 6.56. Found: C, 51.42; H, 6.86. IR (KBr,  $\text{cm}^{-1}$ ): 3004 (w), 2929 (w), 1502 (w), 1443 (m, br), 1395 (m), 1284 (w), 1098 (vs, br), 1056 (vs, br), 971 (m), 860 (w), 520 (w), 430 (s). TOF-MS ( $[\text{M} - \text{BF}_4]^+$ ,  $m/z$ ): calcd for  $\text{C}_{19}\text{H}_{29}\text{Ru}$  359.13073; found 359.12988 (error =  $-2.36\text{ ppm}$ ).

**Synthesis of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-CH}_2\text{CHCHCH}_2)]\text{Cl}$  (2-Cl),  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-CH}_2\text{CHCHCH}=\text{CH}_2)\text{Cl}]$  (5), and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^1\text{-CH}_2\text{CH}=\text{CHCH}=\text{CH}_2)\text{Cl}]_2$  (6).** Reaction of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  with Pentadienyllithium. To a solution of 1,4-pentadiene (100  $\mu\text{L}$ , 0.97 mmol) in THF (2 mL) was added *n*-BuLi (388  $\mu\text{L}$ , 2.5 M in hexanes, 0.97 mmol) and the mixture stirred at  $-78\text{ }^{\circ}\text{C}$ . The solution changed first from colorless to yellow and, upon warming to  $0\text{ }^{\circ}\text{C}$ , then to orange. The orange pentadienyllithium

salt solution was added dropwise to a suspension of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  (0.30 g, 0.45 mmol) in 20 mL of THF at  $-78\text{ }^{\circ}\text{C}$ . The solution was warmed to room temperature and stirred for 20 h. The volatiles were removed under vacuum, and the residue was extracted with THF and passed through Celite to remove the unreacted dimer. The supernatant was purified by silica gel chromatography (1 cm  $\times$  10 cm) using THF as eluent. The orange band was concentrated under vacuum and the residue washed with pentane and diethyl ether to afford an insoluble yellow powder, 5. The soluble fraction was identified spectroscopically as a mixture of 2-Cl, 6, and traces of 5. Complex 5: IR (microscope,  $\text{cm}^{-1}$ ): 3416 (m, br), 3081 (m), 2923 (vs, br), 1938 (m, br), 1817 (w), 1666 (s, br), 1614 (vs), 1565 (s, br), 1444 (vs, br), 1383 (vs, br), 1295 (m), 1266 (m), 1191 (s), 1162 (s), 1070 (vs, br), 1009 (vs, br), 909 (s), 894 (vs), 783 (m), 685 (s, br). HR-EIMS ( $[\text{M}]^+$ ,  $m/z$ ): calcd for  $\text{C}_{17}\text{H}_{25}\text{ClRu}$  366.06882; found 366.06898 (error =  $-0.4\text{ ppm}$ ). HR-ESIMS ( $[\text{M} - \text{Cl}]^+$ ,  $m/z$ ): calcd for  $\text{C}_{17}\text{H}_{25}\text{Ru}$  331.09943; found 331.09965 (error =  $0.7\text{ ppm}$ ).

**Reaction of the Mixture of Compounds 2-Cl, 5, and 6 with AgBF<sub>4</sub>.** In an NMR tube, a mixture of 2-Cl, 5, and 6 in acetone-*d*<sub>6</sub> (0.5 mL) was determined to be in a 5:2:5 ratio, respectively. Approximately 5 mg of AgBF<sub>4</sub> was added in one portion, and immediately a white-gray precipitate of AgCl was observed. After filtration, the solution consisted exclusively of 2-BF<sub>4</sub>.

**Synthesis of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-CH}_2\text{CHCHCH}=\text{CH}_2)\text{Cl}]$  (5),  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{\eta^3\text{-CH}(\text{Me})\text{CHCH}(\text{Me})\text{Cl}\}]$  (7), and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-CH}_2\text{CHCHCH}_2\text{Me})\text{Cl}]$  (8).** Reaction of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  with 1,4-Pentadiene and Na<sub>2</sub>CO<sub>3</sub>. Into a glass reactor equipped with a stir bar were placed  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  (0.20 g, 0.30 mmol), Na<sub>2</sub>CO<sub>3</sub> (0.20 g, 1.89 mmol), EtOH (10 mL), and 1,4-pentadiene (0.124 mL, 1.20 mmol). The reactor was sealed and placed in an oil bath at  $70\text{ }^{\circ}\text{C}$  for 1.75 h. The red solution thus obtained was concentrated under vacuum, and the crude product mixture was extracted with benzene and filtered through Celite. After evaporation of the benzene, the crude mixture was chromatographed through SiO<sub>2</sub> (1.5  $\times$  10 cm). Three bands were collected, using diethyl ether as eluent for the first and second bands, followed by acetone for the third. The colorless, first band afforded free hexamethylbenzene (9.6 mg), while the yellow, second band (37.9 mg) was established spectroscopically to be an inseparable mixture of compounds 5, 7, and 8 in a 1:3:6 ratio, respectively. The third band showed only traces of unidentified products.

**Synthesis of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^2\text{-CH}_2=\text{CH}_2)_2]$ .** This compound has been previously synthesized by Bennett et al.<sup>21</sup> Here, we report an improved synthetic procedure increasing the yield from 37% to 58%. In a Fisher-Porter glass pressure vessel (Andrews Glass Co.), 0.25 g (0.374 mmol) of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$ , 0.20 g (1.89 mmol) of Na<sub>2</sub>CO<sub>3</sub>, and 15 mL of ethanol were placed. The vessel was charged with 60 psig of prepurified ethylene and then placed in an oil bath at  $80\text{ }^{\circ}\text{C}$  for 1 h. The crude reaction mixture was transferred to a Schlenk flask and the solvent evaporated under vacuum. In the drybox, the crude product was extracted with hexane ( $3 \times 5\text{ mL}$ ) and sequentially filtered through Celite ( $3 \times 0.5\text{ cm}$ ) and alumina (Brockmann IV,  $3 \times 0.5\text{ cm}$ ). The solvent was slowly evaporated under vacuum, and the yellowish crystals thus obtained were rinsed with cold pentane ( $-40\text{ }^{\circ}\text{C}$ ,  $3 \times 1\text{ mL}$ ). The pentane was evaporated under reduced pressure, and the procedure was repeated until no more crystals were obtained, giving a total of 0.14 g (0.44 mmol, 58%).

**Synthesis of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})]\text{BF}_4$  (9) and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-CH}_2\text{C}(\text{OH})\text{CHC}(\text{Me})\text{CH}_2)]\text{BF}_4$  (10).** Into a Schlenk flask equipped with a stir bar were placed  $[\text{RuCl}_2(\eta^6\text{-C}_6\text{Me}_6)]_2$  (0.20 g, 0.30 mmol) and AgBF<sub>4</sub> (0.25 g, 1.20 mmol). Acetone (5 mL) was added and the resulting solution stirred at room temperature for 40 min. The precipitate was removed by filtration and rinsed with acetone ( $2 \times 5\text{ mL}$ ). The orange solution thus obtained was transferred to a 50 mL round-bottom flask, and 1,3-

dimethyl-1-trimethylsilyloxy-1,3-butadiene (0.146 g, 0.86 mmol, mixture of isomers) was added. The reaction mixture was stirred for 2 h at room temperature. The solvent was removed under vacuum and the oily yellow product crystallized several times from acetone/diethyl ether at room temperature to give stable yellow crystals (141 mg, 58%), consisting of a 5:1 mixture of **9** and **10**, respectively. If the purification is conducted by repeated silica gel chromatography using  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (9:1), pure **9** is obtained as a yellow powder in 38% yield.

**Synthesis of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})]\text{BF}_4$  (**9**).** In a Schlenk flask equipped with a stir bar, complex **11** (30 mg, 0.07 mmol) was dissolved in acetone (2 mL) and  $\text{AgBF}_4$  (15.5 mg, 0.08 mmol) was added at room temperature. The mixture was stirred for 1.5 h and the silver chloride was removed by filtration through Celite, affording a yellow solution. Single yellow crystals of complex **9** were deposited from acetone/diethyl ether at room temperature (27 mg, 0.06 mmol, 82%). Mp: 241–243 °C. Anal. Calcd for  $\text{C}_{18}\text{H}_{27}\text{OBF}_4\text{Ru}$ : C, 48.34; H, 6.08. Found: C, 47.29; H, 6.02. IR (microscope,  $\text{cm}^{-1}$ ): 3385 (w, br), 3067 (w), 1438 (s, br), 1392 (s), 1279 (w), 1057 (vs, br), 914 (w). HRESI-MS ( $[\text{M}]^+$ ,  $m/z$ ): calcd for  $\text{C}_{18}\text{H}_{27}\text{ORu}$  361.10999; found 361.11037 (error = 1.1).

**Synthesis of Compound  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-exo-syn-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})\text{Cl}]$  (**11**), Method A.** To a THF (250  $\mu\text{L}$ ) solution of diisopropylamine (44  $\mu\text{L}$ , 0.31 mmol) at  $-78^\circ\text{C}$  was added 2.5 M *n*-BuLi (126  $\mu\text{L}$ , 0.31 mmol). The solution was stirred and slowly warmed to room temperature. After 15 min, the solution was cooled to  $-78^\circ\text{C}$  and mesityl oxide (36  $\mu\text{L}$ , 0.31 mmol) was added dropwise. The solution was warmed to room temperature and stirred for 30 min. The resulting solution of the (oxopentadienyl)lithium salt was slowly added dropwise to a cold ( $-78^\circ\text{C}$ ) suspension of  $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)\text{Cl}_2]_2$  (100 mg, 0.15 mmol) in 10 mL of THF. The solution was allowed to reach room temperature and stirred for 20 h, after which the volatiles were removed under vacuum. The product was extracted from the remaining residue using diethyl ether ( $3 \times 5$  mL), and the resulting orange solution was concentrated and chromatographed on  $\text{SiO}_2$  (1.5 cm  $\times$  12 cm column) using diethyl ether as the eluent. The yellow band was collected and the resulting orange solid was crystallized from benzene at room temperature to give 23 mg (0.06 mmol, 19%) of **11** as single red crystals, which do not melt below  $350^\circ\text{C}$ . Anal. Calcd for  $\text{C}_{18}\text{H}_{27}\text{ClORu}$ : C, 54.60; H, 6.87. Found: C, 54.62; H, 7.05. IR (microscope,  $\text{cm}^{-1}$ ): 3052 (w), 2979 (w, br), 2915 (w, br), 1656 (vs), 1477 (s), 1436 (s, br), 1382 (s), 1348 (s), 1296 (w), 1180 (s), 1067 (w), 1026 (s), 959 (w), 918 (w), 902 (w), 873 (s). HR-EIMS ( $[\text{M}]^+$ ,  $m/z$ ): calcd for  $\text{C}_{18}\text{H}_{27}\text{OClRu}$  396.07938; found 396.08029 (error =  $-2.3$ ).

**Method B.** A solution of the (oxopentadienyl)lithium salt was obtained as described in method A and slowly added dropwise to a suspension of  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{pyridine})\text{Cl}_2]$  (**12**) (130 mg, 0.31 mmol) in 10 mL of THF at  $-78^\circ\text{C}$ . The solution was allowed to reach room temperature and stirred for 20 h, followed by heating to reflux for 1 h. The solution was filtered, and the volatiles were removed under vacuum. The product was extracted from the remaining residue using benzene ( $3 \times 5$  mL) and filtered through a Celite pad. The resulting orange solution was concentrated and purified by chromatography on  $\text{SiO}_2$  (1.5 cm  $\times$  10 cm column) using diethyl ether as eluent. The yellow band was collected, affording **11** as an orange powder (22 mg, 0.06 mmol, 19%).

**Synthesis of Compound  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{C}_5\text{H}_5\text{N})\text{Cl}_2]$  (**12**).** In a 50 mL round-bottom flask equipped with a stir bar,  $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)\text{Cl}_2]_2$  (200 mg, 0.30 mmol) was suspended in 15 mL of pyridine. The resulting mixture was heated to reflux for 3 h and then cooled to room temperature. An orange precipitate was obtained upon addition of 50 mL of hexane. The solid was isolated by filtration, washed with hexanes, and dried under vacuum to give **12** as an orange solid (0.215 g, 0.52 mmol, 87%). Compound **12**

was crystallized from  $\text{CH}_2\text{Cl}_2$  at room temperature to give red crystals that do not melt below  $350^\circ\text{C}$ .  $^1\text{H}$  NMR [ $\text{CDCl}_3$ ,  $J(\text{Hz})$ ]:  $\delta$  8.79 (dd, 6.4, 1.4, 2H), 7.69 (tt, 7.6, 1.4, 1H), 7.28 (t, 7.5, 2H), 1.97 (s, 18H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  154.75 (CH), 137.31 (CH), 124.65 (CH), 91.34 ( $\text{C}_6\text{Me}_6$ ), 15.50 ( $\text{C}_6\text{Me}_6$ ). FT-IR (KBr,  $\text{cm}^{-1}$ ): 3036 (m), 2924 (m), 2369 (w), 2028 (w), 1947 (w), 1740 (w), 1647 (w), 1596 (m), 1473 (m), 1444 (vs), 1382 (s), 1212 (m), 1069 (s), 1022 (s), 777 (s), 704 (s), 636 (w), 539 (w), 461 (w). TOF-MS ( $[\text{M} + \text{H}]^+$ ,  $m/z$ ): calcd for  $\text{C}_{17}\text{H}_{24}\text{Cl}_2\text{NRu}$  414.03237; found 414.03157 (error =  $-2.0$ ).

**Synthesis of  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\eta^3\text{-exo-syn-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})\text{-Cl}]$  (**13**) and  $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\eta^3\text{-endo-CH}_2\text{C}(\text{Me})\text{CHC}(\text{Me})\text{O})\text{Cl}]$  (**13-endo**).** The (oxopentadienyl)lithium salt (1.2 equiv), obtained as described for compound **11**, was slowly added dropwise to a suspension of  $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}_2]_2$  (400 mg, 0.80 mmol) in 20 mL of THF at  $-78^\circ\text{C}$ . The solution was allowed to reach room temperature and stirred for 20 h. The solvent was evaporated and the crude reaction mixture extracted with  $\text{CHCl}_3$ , leaving unreactive dimer. The volume of the solvent was reduced and the residue purified by chromatography on  $\text{SiO}_2$  (15  $\times$  1 cm). Two fractions were eluted, the first using THF and the second using acetone. Both fractions contained mixture of compounds, and both need to be chromatographed using the same solvents. Compound **13-exo-syn** was obtained as an orange powder and crystallized from  $\text{CH}_2\text{Cl}_2$  at room temperature (19 mg, 0.06 mmol, 4%). The second compound, assigned as **13-endo**, was obtained in traces and characterized only by  $^1\text{H}$  NMR. Compound **13**: Anal. Calcd for  $\text{C}_{12}\text{H}_{15}\text{OClRu}$ : C, 46.23; H, 4.85. Found: C, 46.06; H, 4.85. IR (microscope,  $\text{cm}^{-1}$ ): 3064 (m), 2962 (m), 1659 (vs), 1477 (s), 1424 (vs, br), 1380 (s), 1355 (s), 1296 (m), 1177 (s), 1049 (m), 1021 (w), 963 (m), 912 (m), 882 (m), 813 (m). HRESI-MS ( $[\text{M}]^+$ ,  $m/z$ ): calcd for  $\text{C}_{12}\text{H}_{15}\text{OClRu}$  311.98550; found 311.98435 (error = 3.7).

**Synthesis of Compounds  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-CH}_2\text{CHCHCHO})]\text{-BF}_4$  (**14**) and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(1\text{-3,5-}\eta\text{-exo-syn-CH}_2\text{CHCHCHO})]_2\text{-}(\text{BF}_4)_2$  (**15**).** Into a Schlenk flask equipped with a stir bar were placed  $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)\text{Cl}_2]_2$  (0.30 g, 0.45 mmol) and  $\text{AgBF}_4$  (0.38 g, 1.95 mmol). Acetone (6 mL) was added, and the mixture was stirred for 1 h. The  $\text{AgCl}$  precipitate was removed by filtration and rinsed with acetone (6 mL). The orange solution thus obtained was transferred to a 50 mL round-bottom flask, and 1-trimethylsilyloxy-1,3-butadiene (0.24 mL, 1.67 mmol) was added. Once the addition was complete, after stirring several minutes, an orange-yellow precipitate was observed. The solid was filtered and dried under vacuum to give dimer **15** in 69% yield (0.26 g, 0.31 mmol). Compound **15** does not melt below  $350^\circ\text{C}$ . Complex **14** was observed in the supernatant by  $^1\text{H}$  NMR spectroscopy, but not isolated. Single crystals of **15** were obtained from  $\text{CH}_3\text{NO}_2/\text{diethyl ether}$ . Anal. Calcd  $\text{C}_{32}\text{H}_{46}\text{O}_2\text{B}_2\text{F}_8\text{Ru}_2$ : C, 45.84; H, 5.53. Found: C 45.66; H, 5.56. IR (KBr,  $\text{cm}^{-1}$ ): 3013 (m), 1669 (m), 1573 (vs, br), 1447 (m, br), 1392 (m, br), 1286 (w), 1203 (s), 1175 (m), 1059 (vs, br), 947 (m), 773 (w), 632 (w), 533 (m, br). TOF-MS ( $[\text{M} - \text{BF}_4]^+$ ,  $m/z$ ): calcd for  $\text{C}_{16}\text{H}_{23}\text{ORu}$  333.07869; found 333.07961 (error = 2.75).

**Synthesis of Compound  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^5\text{-CH}_2\text{CHCHCHO})]$  (**14**).** Complex **15** (100 mg, 0.12 mmol) was placed in a Schlenk flask with a stir bar and dissolved in  $\text{CH}_3\text{NO}_2$  (99.9 + %, 1 mL). The resulting red solution was placed in an oil bath at  $50^\circ\text{C}$  for 5 h without evident change of the solution color. The solution was passed through Celite and crystallized by direct diffusion from  $\text{CH}_3\text{-NO}_2/\text{diethyl ether}$  at room temperature, affording amber crystals along with an oily brown-orange residue. Decantation and drying afforded complex **14** as a microcrystalline brown powder (87 mg, 0.21 mmol, 87%). TOF-MS ( $[\text{M} - \text{BF}_4]^+$ ,  $m/z$ ): calcd for  $\text{C}_{16}\text{H}_{23}\text{-ORu}$  333.07869; found 333.07914 (error = 1.4 ppm).

**Identification of Compounds  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-exo-CH}_2\text{CHCHCHO})(\text{D}_2\text{O})]\text{BF}_4$  (**16**) and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-exo-CH}_2\text{CHCHCHO})(\text{CD}_3\text{CN})]\text{BF}_4$  (**17**).** NMR tubes containing



compound **15** (10 mg, 0.012 mmol) and 0.6 mL of acetone- $d_6$  or nitromethane- $d_3$  were prepared. D<sub>2</sub>O (30  $\mu$ L, 1.66 mmol) was added into each NMR tube, affording  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-oxodienyl})(\text{D}_2\text{O})]\text{-BF}_4$  (**16'**). Addition of CD<sub>3</sub>CN (30  $\mu$ L, 0.58 mmol) to both tubes affords  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-oxodienyl})(\text{CD}_3\text{CN})]\text{BF}_4$  (**17'**). Mass spectrometry of **16** was obtained using **15** in the presence of water [HRESI-MS ( $[\text{M} - \text{BF}_4]^+$ ,  $m/z$ ): calcd for C<sub>16</sub>H<sub>25</sub>O<sub>2</sub>Ru 351.08925; found 351.08959 (error = 1.0 ppm)].

**Synthesis of Compound  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-exo-CH}_2\text{-CHCHCHO})(\text{MeCN})]\text{BF}_4$  (**17**).** Complex **15** (50 mg, 0.06 mmol) was placed in a Schlenk flask with a stir bar and dissolved in 2 mL of CH<sub>3</sub>CN (38.29 mmol). After a few minutes the red solution turned to yellow. The solution was stirred for 10 min, filtered through Celite, and crystallized by indirect (vapor) diffusion, using acetonitrile and diethyl ether. Complex **17** was obtained as a microcrystalline yellow powder in 89% yield (49 mg, 0.11 mmol), mp 180–181 °C. FT-IR (KBr, cm<sup>-1</sup>): 2986 (w), 2930 (w), 2284 (w), 2056 (w), 2035 (w), 1670 (s), 1496 (w), 1450 (w), 1392 (m), 1148 (s), 1059 (vs,br), 946 (w), 883 (w), 799 (w), 618 (w), 521 (m). TOF-MS ( $[\text{M}]^+$ ,  $m/z$ ): calcd for C<sub>18</sub>H<sub>26</sub>NORu 374.10523; found 374.10490 (error = -0.9 ppm).

**Synthesis of Compound  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-exo-CH}_2\text{-CHCHCHO})(\text{EtCN})]\text{BF}_4$  (**18**).** Complex **18** was obtained by stirring dimer **15** (60 mg, 0.07 mmol) in nitromethane (5 mL, reagent grade, 96%) for 12 h at room temperature. During this time, the red solution changed to yellow, and crystallization from nitromethane/diethyl ether afforded a small quantity of **18** as yellow crystals (~20 mg). IR (KBr, cm<sup>-1</sup>):  $\nu_{\text{CO}}$  1669 cm<sup>-1</sup> (vs). TOF-MS ( $[\text{M} - \text{BF}_4]^+$ ,  $m/z$ ): calcd for C<sub>19</sub>H<sub>28</sub>ONRu 388.12089; found 388.12152 (error = 1.62 ppm).

**Identification of Compounds  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-endo-CH}_2\text{CHCH}_2)(\text{CO})]\text{BF}_4$  (**19-endo**) and  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-exo-CH}_2\text{CHCH}_2)(\text{CO})]\text{BF}_4$  (**19-exo**).** In an NMR tube, 10 mg of dimer **15** was dissolved in CD<sub>3</sub>NO<sub>2</sub> (0.6 mL). The NMR tube was placed into an oil bath and heated to 100 °C. After 2 min, the red solution turned yellow, affording complex **14** quantitatively, while after 1 h, a mixture of **19-endo** and **19-exo** was observed in a 3:2 ratio. After 8 h, **19-exo** is observed as the exclusive product. Subsequent crystallization of the sample (CD<sub>3</sub>NO<sub>2</sub>/diethyl ether) gave colorless crystals, which do not melt below 350 °C. In a similar fashion, heating **15** at 50 °C for 2 h affords a mixture of **15** and **14** in a 2:3 ratio; after 13 h, compounds **14** and **19-endo** are observed in a 9:1 ratio; and after 60 h, compounds **14**, **19-endo**, and **19-exo** are observed in a 3:6:1 ratio, respectively. On a larger scale, complex **19-exo** was obtained in very poor yield (~5%) by heating dimer **15** (100 mg) in 1 mL of CH<sub>3</sub>NO<sub>2</sub> for 8 h at 100 °C, which affords mainly decomposition products. **19-exo**: IR (KBr, cm<sup>-1</sup>):  $\nu_{\text{CO}}$  2010 cm<sup>-1</sup> (s). TOF-MS ( $[\text{M} - \text{BF}_4]^+$ ,  $m/z$ ): calcd for C<sub>16</sub>H<sub>23</sub>ORu 333.07869; found 333.07944 (error = 2.24 ppm).

**Synthesis of Compound  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\eta^3\text{-exo-CH}_2\text{-CHCHCHO})\text{Cl}]\text{BF}_4$  (**20**).** In a 50 mL round-bottom flask equipped with a stir bar, complex **15** (100 mg, 0.12 mmol) was suspended in 6 mL of acetone. Sodium chloride (20 mg, 0.34 mmol) in 0.24 mL of H<sub>2</sub>O was added. The reaction mixture was stirred for 2 h and the solvent removed under vacuum. The product was extracted with benzene (3  $\times$  5 mL), and the volatiles were evaporated. Complex **20** was obtained as an orange powder after drying under vacuum (0.083 g, 0.23 mmol, 94%). Pure red crystals of **20** can be obtained by slow evaporation of THF at room temperature, mp (dec) 182–185 °C. Anal. Calcd for C<sub>16</sub>H<sub>23</sub>ClORu: C, 52.24; H, 6.30.

Found: C, 52.51; H, 6.31. IR (microscope, cm<sup>-1</sup>): 3319 (w), 3066 (s), 2919 (s, br), 2802 (s), 2731 (s), 2269 (w), 2110 (w), 1940 (w), 1815 (w), 1666 (vs), 1490 (s), 1441 (s, br), 1390 (s, br), 1136 (s), 1007 (s, br), 907 (s). HRESI-MS ( $[\text{M} + \text{H}]^+$ ,  $m/z$ ): calcd for C<sub>16</sub>H<sub>24</sub>-OClRu 369.05537; found 369.05553 (error = 0.4 ppm).

**Reaction of Complex **20** and AgBF<sub>4</sub>.** To a solution of complex **20** (35 mg, 0.10 mmol) in acetone (2 mL) at -110 °C was added AgBF<sub>4</sub> (18.5 mg, 0.13 mmol) in 1 mL of acetone. The solution was slowly warmed to room temperature, resulting in an orange solution and a white precipitate. After filtration and evaporation under vacuum, the solid orange residue was washed with acetone (3  $\times$  3 mL), affording dimer **15** (20 mg, 0.06 mmol) as an insoluble orange solid, along with an orange solution of residual **20** and several unidentified byproducts.

**Synthesis of Compound  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{MeCN})_3](\text{BF}_4)_2$ .** Into a Schlenk flask equipped with a stir bar were placed  $[\text{Ru}(\eta^6\text{-C}_6\text{Me}_6)\text{Cl}_2]_2$  (0.30 g, 0.45 mmol) and AgBF<sub>4</sub> (0.35 g, 1.80 mmol). Acetonitrile (10 mL) was added, and the mixture was stirred for 40 min. The yellow solution thus obtained was filtered through Celite, and the solvent diminished until approximately 1 mL. Addition of 5 mL of diethyl ether affords a yellow powder, which was filtered and dried under vacuum to give compound  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{MeCN})_3](\text{BF}_4)_2$  in 97% yield (0.485 g, 0.87 mmol). <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$  2.21 (s, 18H), 2.45 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>-CN):  $\delta$  16.49 (C<sub>6</sub>Me<sub>6</sub>), 98.83 (C<sub>6</sub>Me<sub>6</sub>), 4.39 (MeCN), 128.34 (MeCN) (coord. CD<sub>3</sub>CN  $\delta$  4.00).

## Conclusions

In summary, reasonably general methodology for the synthesis of cationic ruthenium(II)  $\eta^5$ -pentadienyl complexes stabilized by the  $(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}$  fragment has been developed, using the strongly electrophilic labile dication  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{acetone})_3]^{2+}$  and weakly nucleophilic dienyl derivatives of group 14 metals (Si, Sn). Although a similar strategy for the synthesis of the corresponding  $\eta^5$ -oxopentadienyl derivatives is complicated by competition from alternative bonding modes, the first examples of cationic  $\eta^5$ -oxopentadienyl complexes of ruthenium have also been prepared and fully characterized. The reactivity of the hetero-substituted polyenyl fragment in this unique coordination environment will be reported in due course.

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**Supporting Information Available:** Tables of crystallographic data, including atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and least-squares planes for compounds **2-BF<sub>4</sub>**, **4**, **9**, **11**, **13**, **15**, and **19-exo**. NMR spectra of **2-Cl**, **5–10**, **14** and isomers of 2,4-dimethyl-1-trimethylstannyl-2,4-pentadiene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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