Structure and Chemistry of the Complex Tetrakis(η^5-pentamethylcyclopentadienyl)tetrakis(μ_3-chloro)tetraruthenium(II): A Useful Precursor to (Pentamethylcyclopentadienyl)ruthenium(0), -(II), and -(IV) Complexes[†]

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A single-crystal X-ray structural analysis of the complex $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ (**1**, $Cp^* = \eta^5\text{-}C_5(CH_3)_5$) has been performed (triclinic, $P\bar{1}$ (No. 2); a = 11.281 (5); b = 11.354 (4); c = 18.846 (5) Å; α = 82.20 (2)°, β = 82.03 (3)°, γ = 65.45 (4)°; V = 2166.3 Å^3, Z = 2). The complex contains a distorted cubic array of ruthenium and chlorine atoms. The complex **1** is a useful precursor to Ru(0), Ru(II), and Ru(IV) pentamethylcyclopentadienyl complexes. Reaction of **1** with donor ligands yields Cp^*RuL_2Cl complexes (L = CO, $P(CH_3)_3$). With dienes, **1** yields the complexes $Cp^*Ru(\eta^4\text{-diene})Cl$ (diene = 1,3-butadiene, 1,3-pentadiene, *trans*-2,*trans*-4-hexadiene, 2,3-dimethyl-1,3-butadiene, 2,3-diphenyl-1,3-butadiene, 1,3-cyclohexadiene, 1,3-cycloheptadiene, 1,5-cyclooctadiene, norbornadiene) which in turn can be reduced with lithium to yield the corresponding anionic diene complexes $Cp^*Ru(\eta^4\text{-diene})^-Li^+\cdot DME$ (DME = 1,2-dimethoxyethane). The complex $[Cp^*Ru(\mu_3\text{-}I)]_4$ has also been prepared and reacts with 1,3-butadiene to yield $Cp^*Ru(\eta^4\text{-}s\text{-}cis\text{-}1,3\text{-butadiene})I$, which has been structurally characterized by a single-crystal X-ray analysis (monoclinic *b*, $P2_1/c$ (No. 14); a = 7.177 (2); b = 14.362 (3); c = 13.788 (2) Å; β = 93.39 (1)°; V = 1418.7 Å^3, Z = 4). Reaction of **1** with ethylene yields the complex $[Cp^*Ru(\eta^2\text{-}C_2H_4)Cl]_x$, which can be converted to the complex $Cp^*Ru(\eta^2\text{-}C_2H_4)_2Li$. With allyl chloride, **1** yields the oxidative addition product $Cp^*Ru(\eta^3\text{-}C_3H_5)Cl_2$.

Introduction

We have reported previously the synthesis of the complex $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$) (**1**) and its conversion to the acetonitrile complex $[Cp^*Ru(CH_3CN)_3]^+O_3SCF_3^-$ (**2**).[1] Complex **2** has been shown to be exceptionally useful in the preparation of ruthenium arene complexes.[1] Here we describe the structure of intermediate **1** and its use in the preparation of other Cp*Ru compounds. Our initial interest in this area was to find routes for the synthesis of ruthenium anions of the type $Cp^*Ru(\eta^4\text{-diene})^-$ and $Cp^*Ru(\eta^2\text{-}C_2H_4)_2^-$ and investigate their chemistry. Using **1** as a precursor, we have succeeded in synthesizing these anions as described here. The reactions illustrated in this paper show that complex **1** should be useful in the preparation of many other (pentamethylcyclopentadienyl)ruthenium complexes.[2–4] Tilley and co-workers[3b] have recently used our complex **1** in the preparation of Ru(II) alkoxides and phosphines, and Koelle et al.[5] as well as Chaudret et al.[6] have reported some of their work in this area.

Results and Discussion

Synthesis and Structure of $[Cp^*Ru(\mu_3\text{-}Cl)]_4$. As we previously reported,[1] complex **1** can be prepared by addition of 1 equiv of lithium triethylborohydride to Cp^*RuCl_2[2,3a,5] (eq 1). A transient blue–green color was

$$(1/x)(Cp^*RuCl_2)_x + (C_2H_5)_3BH^-Li^+ \xrightarrow[-B(C_2H_5)_3]{-LiCl} [(1/x)[Cp^*Ru(H)Cl]_x] \xrightarrow{-{}^1/_2H_2} {}^1/_4\underset{\mathbf{1}}{[Cp^*Ru(\mu_3\text{-}Cl)]_4} \quad (1)$$

observed in solution upon initial addition of the triethylborohydride solution and is presumably due to the presence of a mixed-valent Ru(II)–Ru(III) complex. (The same color develops if 1 equiv of **1** is added to 1 equiv of Cp^*RuCl_2, and Koelle and co-workers[5b] have reported the isolation of a mixed-valent species formulated as

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[†] Contribution No. 4924.

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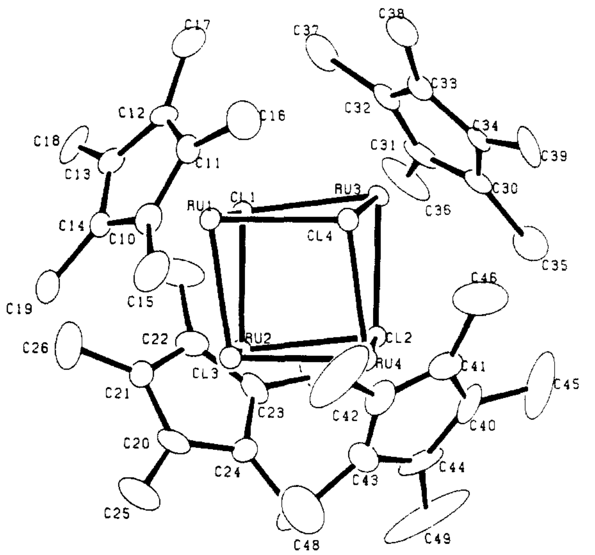


Figure 1. ORTEP drawing of $[Cp^*Ru(\mu_3\text{-}Cl)]_4$.

$Cp^*{}_2Ru_2Cl_3$). The complex 1 is slightly soluble in THF and is only very slightly soluble in hexane. It dissolves in CH_3CN to yield a yellow solution of the $Cp^*Ru(CH_3CN)_3{}^+$ cation with Cl^- as the counteranion. Removal of CH_3CN from this solution in vacuo reforms the complex 1. The chloride can be metathesized with iodide by addition of sodium iodide to a CH_3CN solution of 1 which precipitates NaCl. After filtration and removal of solvent, the iodide analogue $[Cp^*Ru(\mu_3\text{-}I)]_4$ is obtained (eq 2). As we have

$$\underset{1}{[Cp^*Ru(\mu_3\text{-}Cl)]_4} + 4NaI \xrightarrow[-4NaCl]{CH_3CN} [Cp^*Ru(\mu_3\text{-}I)]_4 \quad (2)$$

reported elsewhere, addition of AgO_3SCF_3 to an acetonitrile solution of $Cp^*Ru(CH_3CN)_3{}^+Cl^-$ produces the stable complex $Cp^*Ru(CH_3CN)_3{}^+O_3SCF_3{}^-$.[1]

Single crystals of 1 were grown by performing the reaction shown in eq 1 in a flask without stirring and then allowing the mixture to stand. The results of a single-crystal X-ray analysis of this complex are displayed in Figure 1, and two views of the central core of the molecule are shown in Figure 2.[7] Tables V and VI list the bond distances and bond angles obtained for 1. The analysis reveals that in the solid state the complex is tetrameric and contains a distorted cubic array of four Ru and four Cl atoms. A $C_5(CH_3)_5$ ligand (which is not significantly slipped) is bound in a η^5 fashion to each Ru atom. The average Cp*(centroid)–Ru distance is 1.720 (3) Å, which is somewhat shorter than the Cp*Ru distances reported elsewhere.[1] There is no evidence of metal–metal bonding within the cluster as the shortest Ru–Ru distance is 3.776 (2) Å. The array of the Ru and Cl atoms is distorted in such a way that it approximates T_d point group symmetry as can be seen by inspection of Figure 2. The plane defined by Ru1, Cl1, and Cl3 makes an angle of 168.3 (1)° with the plane defined by Ru2, Cl1, and Cl3; the plane Ru3–Ru4–Cl2 is bent 166.9 (1)° relative to the plane Ru3–Ru4–Cl4.

The molecule 1 is a member of the class of complexes with the general formula $[(\eta^5\text{-}C_5R_5)M(\mu_3\text{-}E)]_4$, which contain cubic central cores with or without metal–metal bonding.[8] This structure is also related to the ruthenium arene hydroxo derivatives $[(\eta^6\text{-arene})Ru(\mu_3\text{-}OH)]_4{}^{4+}$, which are isoelectronic with $[Cp^*Ru(\mu_3\text{-}Cl)]_4$.[9]

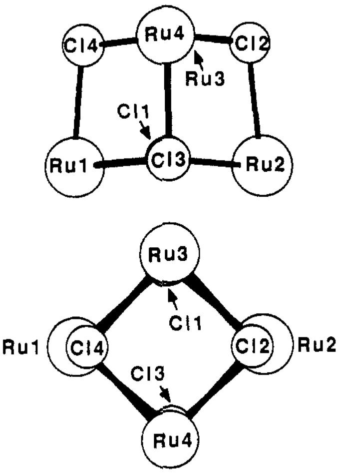


Figure 2. Pseudocubic Ru_4Cl_4 core of $[Cp^*Ru(\mu_3\text{-}Cl)]_4$.

Reaction of 1 with CO, PMe$_3$, and Dienes and the Structure of Cp*Ru(η^4-1,3-butadiene)I. Even though 1 is a cluster, the Ru–Cl bonds of 1 are quite labile, and the cluster is easily broken up by donor ligands. For example, bubbling carbon monoxide through a solution of $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ yields the known complex $Cp^*Ru(CO)_2Cl$ in essentially quantitative yield, a reaction also noted elsewhere[5b] (eq 3). This reaction represents a convenient

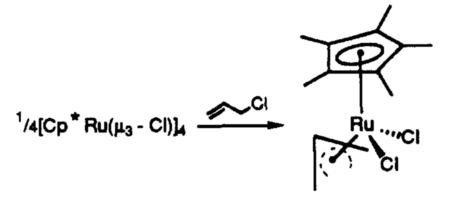
$$\tfrac{1}{4}1 + 2L \xrightarrow{THF} Cp^*RuL_2Cl \quad (3)$$
$$L = CO, PMe_3$$

synthetic route to Cp*Ru carbonyl-containing complexes and is an improvement over routes starting from $Ru_3(CO)_{12}$.[10] For example, $Cp^*Ru(CO)_2Cl$ is readily converted to the known hydride derivative $Cp^*Ru(CO)_2H$ by reaction with lithium triethylborohydride (eq 4), which in turn is known to be a source of the complex $[Cp^*Ru(CO)_2]_2$.[10]

$$Cp^*Ru(CO)_2Cl \xrightarrow[THF]{Et_3BH^-Li^+} Cp^*Ru(CO)_2H \quad (4)$$

Addition of trimethylphosphine to 1 yields the previously reported complex $Cp^*Ru[P(CH_3)_3]_2Cl$, which has also been prepared by Tilley et al. by the reaction of PMe_3 with the Ru(III) derivative $(Cp^*RuCl_2)_x$.[3a] It is possible that in the latter reaction, PMe_3 reduces $(Cp^*RuCl_2)_x$ to 1 initially, which then reacts to yield $Cp^*Ru[P(CH_3)_3]_2Cl$. Tilley et al. have also used our complex in the preparation of coordinatively unsaturated $Cp^*Ru(PR_3)Cl$ derivatives.[3]

A number of known reactions with $(Cp^*RuCl_2)_x$ undoubtedly proceed through the intermediacy of 1. For example, we have carried out the reaction of allyl chloride with 1 in THF, which instantaneously reacts to form the Ru(IV) allyl complex $Cp^*Ru(\eta^3\text{-}C_3H_5)Cl_2$ (eq 5). This



(5)

complex had previously been prepared by Itoh and co-

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Table I. ^{1}H NMR Data for Cp*Ru(η^4-diene)Cl Complexes[a]

compound	δ Cp*	δ diene
Cp*Ru(η^4-1,3-butadiene)I	1.79 (s, 15 H)	1.56 (m, 2 H); 2.70 (m, 2 H); 4.28 (m, 2 H)
Cp*Ru(η^4-1,3-butadiene)Cl	1.62 (s, 15 H)	1.34 (m, 2 H); 3.08 (m, 2 H); 4.54 (m, 2 H)
Cp*Ru(η^4-*trans*-1,3-pentadiene)Cl	1.60 (s, 15 H)	1.22 (ddd, 1 H, J = 10.6, 0.7, 1.6 Hz); 1.49 (d, 3 H, J = 6.3 Hz); 2.04 (ddq, 1 H, J = 10.3, 6.3, 0.7 Hz); 2.83 (dd, 1 H, J = 7.4, 1.6 Hz); 4.32 (dddd, 1 H, 10.6, 7.4, 5.5, 0.7 Hz); 4.62 (ddd, 1 H, J = 5.5, 10.3, 0.7 Hz)
Cp*Ru(η^4-*trans*-2,*trans*-4-hexadiene)Cl	1.59 (s, 15 H)	1.47 (d, 6 H, J = 6.3 Hz); 1.89 (quintet, 2 H, J = 6.2 Hz); 4.43 (d, 2 H, J = 8.0[b])
Cp*Ru(η^4-2,3-dimethyl-1,3-butadiene)Cl	1.61 (s, 15 H)	1.20 (d, 2 H, J = 1.7 Hz); 1.96 (s, 6 H); 3.04 (d, 2 H, J = 1.7 Hz)
Cp*Ru(η^4-1,3-cyclohexadiene)Cl	1.62 (s, 15 H)	1.27 (m, 2 H); 1.74 (m, 2 H); 3.41 (m, 2 H); 4.18 (m, 2 H)
Cp*Ru(η^4-1,3-cycloheptadiene)Cl	1.55 (s, 15 H)	0.87 (q of t, 1 H, J = 13.0, 3.7 Hz); 1.17 (d of m, 1 H, J = 13.0 Hz); 1.76 (d of m, 2 H, J = 16.6);[c] 2.16 (dddd, 2 H, J = 16.6, 13.0, 3.8, 1.0); 3.53 (m, 2 H); 3.82 (m, 2 H)
Cp*Ru(η^4-1,5-cyclooctadiene)Cl	1.56 (s, 15 H)	1.82 (m, 2 H); 1.92 (m, 2 H); 2.13 (m, 2 H); 2.54 (m, 2 H); 3.65 (m, 2 H); 3.95 (m, 2 H)
Cp*Ru(η^4-2,5-norbornadiene)Cl	1.57 (s, 15 H)	1.21 (t, 2 H, J = 1.4 Hz); 3.51 (m, 1 H); 3.56 (t, 2 H, J = 4.0 Hz); 3.76 (m, 1 H); 3.92 (t, 2 H, J = 4.0 Hz)

[a] Reported in ppm from tetramethylsilane (300 MHz at 25 °C) in THF-d_8 unless indicated otherwise (s = singlet, d = doublet, t = triplet, q = quartet, sh = shoulder, br = broad, m = multiplet). [b] Second-order splitting was apparent due to the AA′MM′X$_6$ spin system. [c] Overlaps with solvent THF-d_7 resonance.

Table II. ^{13}C NMR Data for Cp*Ru(η^4-diene)Cl Complexes[a,b]

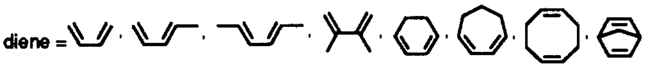
compound	δ Cp*	δ diene
Cp*Ru(η^4-1,3-butadiene)I	10.8 (q, 127); 94.8 (s)	46.4 (t, 162); 88.5 (d, 164)
Cp*Ru(η^4-1,3-butadiene)Cl	9.3 (q, 128); 95.8 (s)	54.0 (t, 164); 92.3 (d, 163)
Cp*Ru(η^4-*trans*-1,3-pentadiene)Cl	9.5 (q, 127); 95.1 (s)	17.2 (q, 125); 52.1 (t, 161); 72.0 (d, 161); 88.3 (d, 163); 94.9 (d, 161)
Cp*Ru(η^4-*trans*-2,*trans*-4-hexadiene)Cl	9.8 (q, 127); 94.0 (s)	17.5 (q, 126); 69.2 (d, 161); 92.2 (d, 165)
Cp*Ru(η^4-2,3-dimethyl-1,3-butadiene)Cl	9.4 (q, 127); 96.0 (s)	18.7 (q, 127); 55.3 (t, 160); 101.5 (s)
Cp*Ru(η^4-1,3-cyclohexadiene)Cl	9.4 (q, 127); 96.4 (s)	20.7 (t, 129); 66.3 (d, 165); 83.6 (d, 167)
Cp*Ru(η^4-1,3-cycloheptadiene)Cl[c]	9.3 (q, 128); 95.5 (s)	20.5 (t, 131); 66.3 (d, 159); 82.9 (d, 168)
Cp*Ru(η^4-1,5-cyclooctadiene)Cl	9.5 (q, 128); 96.6 (s)	29.5 (t, 129); 31.8 (t, 129); 83.5 (d, 153); 84.3 (d, 159)
Cp*Ru(η^4-2,5-norbornadiene)Cl	9.8 (q, 127); 95.4 (s)	47.9 (d, 152); 51.8 (d, 150); 54.0 (d, 174); 61.3 (t, 131); 70.2 (d, 181)

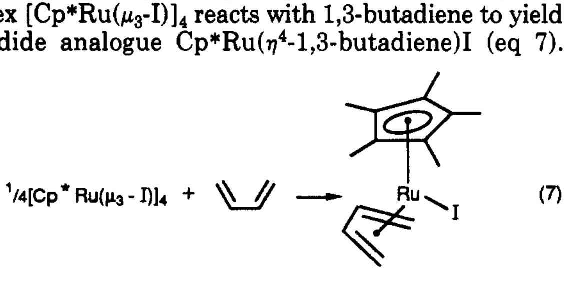
[a] Reported in ppm from tetramethylsilane (75.5 MHz at 25 °C) in THF-d_8 unless indicated otherwise (s = singlet, d = doublet, t = triplet, q = quartet); numbers in parentheses are C–H coupling constants (hertz) unless otherwise specified. Other small two-bond ^{13}C–C–^{1}H couplings (<8 Hz) observed for some of the diene resonances are not reported. [b] Data were obtained from proton-decoupled and proton gated decoupled spectra. [c] Data obtained in C$_6$D$_6$.

workers by reaction of allyl chloride with (Cp*RuCl$_2$)$_x$,[11] and this reaction has been confirmed by Koelle et al.[5b] Gassman and co-workers[12] have recently prepared mixed ruthenocenes from (Cp*RuCl$_2$)$_x$, and 1 is a probable intermediate in these reactions as well.

The complex 1 reacts readily with 1,3-butadiene, 1,3-pentadiene, *trans*-2,*trans*-4-hexadiene, 2,3-dimethyl-1,3-butadiene, 1,3-cyclohexadiene, 1,3-cycloheptadiene, 1,5-cyclooctadiene, and norbornadiene in THF to yield the corresponding Cp*Ru(η^4-diene)Cl complexes in high yield (eq 6). The 1,5-cyclooctadiene and norbornadiene complexes have been reported previously.[2,3a,5b] Similarly, the complex [Cp*Ru(μ_3-I)]$_4$ reacts with 1,3-butadiene to yield the iodide analogue Cp*Ru(η^4-1,3-butadiene)I (eq 7).

$$^1/_4 1 + \text{diene} \longrightarrow \text{Cp}^*\text{Ru}(\eta^4\text{-diene})\text{Cl} \qquad (6)$$





These yellow–orange complexes are readily isolated as crystalline solids that in general are quite soluble in THF but only slightly soluble in hexane. Spectroscopic data for these complexes can be found in Tables I and II.

In a special case, it was found that the product of the reaction of 2,3-diphenyl-1,3-butadiene with 1 was unstable in THF. Therefore the reaction was carried out in diethyl ether in which the product was less soluble and decomposition was slower. The isolated product when dissolved in toluene-d_8 and examined immediately by ^{1}H NMR spectroscopy has resonances due to free 2,3-diphenyl-1,3-butadiene (doublets at δ 5.27 and 5.42 with J = 1.7 Hz), as well as two singlets due to two Cp*Ru-containing products (δ 1.13 and 1.19 in a ratio of ca. 1:1.1, respectively). Besides resonances in the aromatic portion of the spectrum, there are six singlets that are assignable to coordinated 2,3-diphenyl-1,3-butadiene ligands at δ 3.30 (1 H), 3.73 (1 H), 3.79 (1 H), and 4.03 (1 H) (associated with the Cp* resonance at 1.19 (15 H)) and at δ 4.18 (2 H), and 4.37 (2 H) (associated with the Cp* resonance at δ 1.13 (15 H)). These two sets of resonances are assigned to the isomeric complexes Cp*Ru(*s-trans*-η^4-2,3-diphenyl-1,3-butadiene)Cl and Cp*Ru(*s-cis*-η^4-2,3-diphenyl-1,3-butadiene)Cl, respectively (eq 8). Upon standing at room temperature for 2 h, the two complexes were observed to decompose at different rates with the s-cis isomer being almost completely decomposed and the s-trans isomer significantly decreased in amount. There is also an increase in the amount of uncoordinated 2,3-diphenyl-1,3-butadiene. Attempts to recrystallize this product led to decomposition, and the isomeric mixture was therefore used as obtained for further reaction. Dissolution of the

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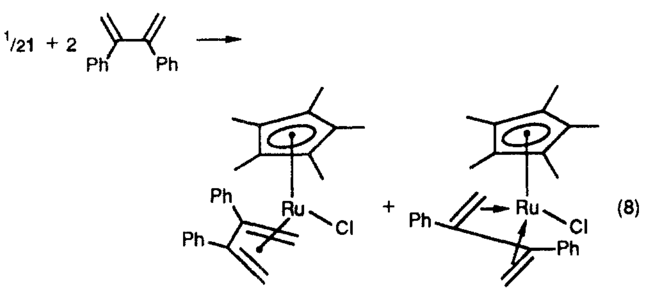


(8)

decomposition product in CD_3NO_2 suggests that the Cp*Ru groups have reacted with the phenyl groups of 2,3-diphenyl-1,3-butadiene to form cationic arene complexes. This is not surprising considering the affinity Cp^*Ru^+ has for aromatic rings.[1] These decomposition products were not fully characterized however. The instability of this complex is probably steric in origin due to unfavorable interaction between the phenyl groups of the butadiene ligand and the Cp* and chloride ligands. The slightly higher stability of the s-trans over the s-cis isomer may be due to the more favorable arrangement of the phenyl groups with respect to one another.

A single-crystal X-ray structural analysis has been performed on the complex $Cp^*Ru(\eta^4\text{-}1,3\text{-butadiene})I$.[6] An ORTEP drawing of these results is presented in Figure 3, and an alternate view of the molecule is presented in Figure 4. Bond lengths and bond angles determined for this complex are given in Tables VII and VIII. The molecule contains a $C_5(CH_3)_5$ ligand bound in a η^5 fashion to the ruthenium atom with the Cp*(centroid)–Ru1 distance being 1.857 (3) Å. Note that this distance is 0.13 Å longer than the corresponding distance in the structure of **1**. This can be attributed in part to the stronger trans influence of the butadiene ligand relative to the weakly bound triply bridging Cl atoms of **1**. An *s-cis*-1,3-butadiene ligand is bound in a η^4 fashion to the Ru1 atom with the butadiene(centroid)–Ru1 distance being 1.778 (3) Å. The terminal methylene groups of the diene are directed towards the iodide substituent. The Ru1–I1 distance of 2.7342 (4) Å is in the range of other reported Ru–I bonds (e.g., Ru–I = 2.732 (1) Å in $(\eta^6\text{-}C_6H_6)(\eta^3\text{-}C_3H_5)RuI$[13]). Angles subtended about Ru1 are as follows: Cp*(centroid)–Ru1–butadiene(centroid) = 142.0°, Cp*(centroid)–Ru–I1 = 116.0°, and butadiene(centroid)–Ru1–I1 = 102.1°.

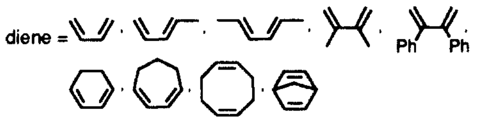
The complex **1** also reacts with ethylene at 60 psi to yield a monosubstituted ethylene complex $[Cp^*Ru(\eta^2\text{-}C_2H_4)Cl]_x$ (eq 9). We have not been able to isolate this complex free

$$\tfrac{1}{4}\mathbf{1} \xrightleftharpoons[\text{DME}]{C_2H_4\text{ (60 psi)}} (1/x)[Cp^*Ru(\eta\text{-}C_2H_4)Cl]_x \qquad (9)$$

of the tetramer **1**, which suggests this reaction is reversible to some extent. This complex is probably oligomeric, although the exact structure cannot be determined from the data at hand.

Synthesis of Anionic Diene and Ethylene Complexes. The Ru(II) diene complexes reported above can be reduced with lithium powder in THF or DME to yield anionic Ru(0) complexes of the general formula $Cp^*Ru(\eta^4\text{-diene})^-Li^+\cdot DME$ following workup in the presence of DME (eq 10). By integration of the ^1H NMR spectra, each of these salts was found to contain 1.00 ± 0.05 molecules of DME per anion which is presumably coordinated to the lithium ion. The yields reported in the Experimental Section are based on this formulation, which

$$Cp^*Ru(\eta^4\text{-diene})Cl \xrightarrow[\text{DME, -60 °C}]{\text{Li}} Cp^*Ru(\eta^4\text{-diene})Li\cdot DME \qquad (10)$$



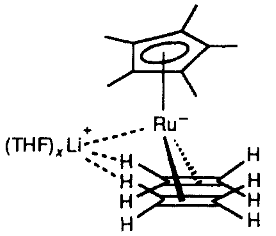
is also supported by the elemental analytical data obtained for $Cp^*Ru(\eta^4\text{-cyclohexadiene})Li\cdot DME$. All of the complexes were isolated as extremely air-sensitive solids. The ^1H NMR and ^{13}C NMR data for these complexes are presented in Tables III and IV. Except for $Cp^*Ru(\eta^4\text{-norbornadiene})Li\cdot DME$, all of these anionic diene complexes are thermally stable when heated in THF-d_8 solution at 60 °C for hours with no sign of decomposition. The complex $Cp^*Ru(\eta^4\text{-norbornadiene})Li\cdot DME$ when heated rearranges slowly and cleanly to another anionic complex that has not been structurally identified as yet.

Attempts to prepare the ethylene substituted anion $Cp^*Ru(\eta^2\text{-}C_2H_4)_2^-$ by reduction of $\{Cp^*Ru(\eta^2\text{-}C_2H_4)Cl\}_x$ with lithium metal under 1 atm of ethylene gas gave only very low yields of the desired product. Thus an alternative method was developed. We reasoned that addition of 2 equiv of ethyllithium to $[Cp^*Ru(\eta^2\text{-}C_2H_4)Cl]_x$ would proceed by first producing the coordinatively unsaturated ethyl–ethylene derivative $Cp^*Ru(C_2H_5)(\eta^2\text{-}C_2H_4)$. This species should undergo β-hydride elimination to yield the intermediate $Cp^*Ru(\eta^2\text{-}C_2H_4)_2H$. Deprotonation of this hydride by the second equivalent of ethyllithium should then lead to the anion $Cp^*Ru(\eta^2\text{-}C_2H_4)_2^-$. When this reaction was carried out under an atmosphere of ethylene, the complex $Cp^*Ru(\eta^2\text{-}C_2H_4)_2^-Li^+$ could then be isolated in 58% yield (eq 11). In contrast to the diene complexes,

$$(1/x)[Cp^*Ru(\eta\text{-}C_2H_4)Cl]_x \xrightarrow{\text{EtLi}} [Cp^*Ru(\eta\text{-}C_2H_4)C_2H_5] \rightarrow [Cp^*Ru(\eta\text{-}C_2H_4)_2H] \xrightarrow{\text{EtLi}} [Cp^*Ru(\eta\text{-}C_2H_4)_2]^-Li^+ \qquad (11)$$

DME does not bind tightly to the lithium counterion in this complex, and the majority of DME was removed from the solid lithium salt by drying in vacuo.

These anionic ruthenium complexes are isoelectronic with the complexes $CpFe(\eta^4\text{-}1,5\text{-cyclooctadiene})Li\cdot TMEDA$ and $CpFe(\eta^2\text{-}C_2H_4)_2Li\cdot TMEDA$ which have been prepared by Jonas and co-workers.[14] In some of their reported studies, these workers had observed ion-pairing phenomena in solution between lithium and the anionic alkene complexes. We have also observed evidence of this phenomenon in some of our ruthenium complexes. The complex $Cp^*Ru(\eta^2\text{-}C_2H_4)_2^-Li^+$ in THF-d_8 solution at low temperature exhibits NMR spectra interpretable in terms of ion pairing between lithium and the ends of each of the ethylene ligands as shown by structure A. Thus at room



A

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[13] Andrianov, V. G.; Lutsenko, Z. L.; Rubezhov, A. Z.; Struchkov, Y. T. *Koord. Khim.* **1982**, *8*, 111-116.

[14] (a) Jonas, K. *Angew Chem.* **1985**, *97*, 292-307. (b) Jonas, K. *Pure Appl. Chem.* **1984**, *56*, 63-80. (c) Jonas, K. *Adv. Organomet. Chem.* **1981**, *19*, 97-122. (d) Jonas, K.; Schieferstein, L. *Angew. Chem.* **1979**, *91*, 590. (e) Jonas, K.; Schieferstein, L.; Krueger, C.; Tsay, Y.-H. *Angew. Chem.* **1979**, *91*, 590-591.

Table III. ^{1}H NMR Data for Cp*Ru(η^4-diene)Li•DME Complexes[a]

compound	δ Cp*	 diene	 DME
Cp*Ru(η^4-1,3-butadiene)Li·DME	1.87 (s, 15 H)	−2.35 (br, 2 H); 0.64 (m, 2 H); 3.38 (m, 2 H)	3.27 (s, 6 H); 3.43 (s, 4 H)
Cp*Ru(η^4-*trans*-1,3-pentadiene)Li·DME	1.85 (s, 15 H)	−2.60 (br, 1 H); −1.51 (quintet, 1 H, J = 5.0 Hz); 0.53 (d, 1 H, J = 5.0 Hz); 1.12 (d, 3 H, J = 5.9 Hz); 3.12 (t, 1 H, 4.2 Hz); 3.29 (1 H)[b]	3.27 (s, 6 H); 3.42 (s, 4 H)
Cp*Ru(η^4-*trans*-2,*trans*-4-hexadiene)Li·DME[c]	1.73 (s, 15 H)[d]	−1.96 (br, 2 H);[d] 1.17 (d, 3 H, J = 5.0 Hz);[d] 2.93 (br m, 2 H)[d]	3.27 (s, 6 H); 3.42 (s, 4 H)
	1.83 (s, 15 H)	−1.27 (br, 2 H); 1.10 (d, 3 H, J = 5.0 Hz); 3.03 (br m, 2 H)	
Cp*Ru(η^4-2,3-dimethyl-1,3-butadiene)Li·DME	1.77 (s, 15 H)	−2.40 (br, 2 H); 0.48 (d, 2 H, J = 1.7 Hz); 1.67 (s, 6 H, CH$_3$)	3.27 (s, 6 H); 3.43 (s, 4 H)
Cp*Ru(η^4-2,3-diphenyl-1,3-butadiene)Li·DME	1.69 (s, 15 H)	−1.66 (s, 2 H); 1.15 (s, 2 H); 6.79 (m, 2 H); 6.88 (m, 4 H); 7.00 (m, 4 H)	3.27 (s, 6 H); 3.43 (s, 4 H)
Cp*Ru(η^4-1,3-cyclohexadiene)Li·DME	1.86 (s, 15 H)	0.99 (m, 2 H, CH$_2$); 1.25 (m, 2 H, CH$_2$); 1.62 (m, 2 H); 3.35 (m, 2 H)	3.27 (s, 6 H); 3.42 (s, 4 H)
Cp*Ru(η^4-1,3-cycloheptadiene)Li·DME	1.86 (s, 15 H)	0.68 (m, 3 H); 1.09 (m, 1 H); 1.22 (m, 2 H); 1.82–1.74 (m, 2 H); 3.39 (m, 2 H)	3.27 (s, 6 H); 3.42 (s, 4 H)
Cp*Ru(η^4-1,5-cyclooctadiene)Li·DME	1.70 (s, 15 H)[e]	1.52, 1.60, 1.67,[e] 1.78 (m's, 12 H)	3.27 (s, 6 H); 3.43 (s, 4 H)
Cp*Ru(η^4-2,5-norbornadiene)Li·DME	1.79 (s, 15 H)	0.74 (m, 2 H); 1.00 (m, 4 H); 3.21 (m, 2 H)	3.27 (s, 6 H); 3.43 (s, 4 H)

[a] Reported in ppm from tetramethylsilane (300 MHz at 25 °C) in THF-d_8 unless indicated otherwise (s = singlet, d = doublet, t = triplet, q = quartet, sh = shoulder, br = broad, m = multiplet). [b] Overlap with DME resonance. [c] Data reported for 0.075 M solution. [d] Resonances for major species at this concentration. [e] Cp* singlet and 1.67 multiplet overlapping.

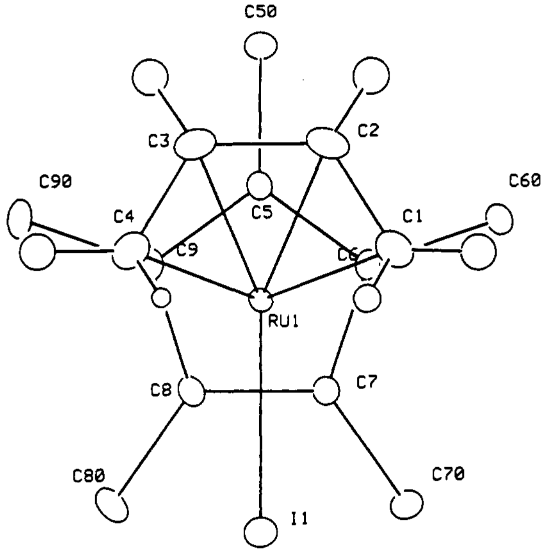


Figure 3. ORTEP drawing of Cp*Ru(η^4-1,3-butadiene)I.

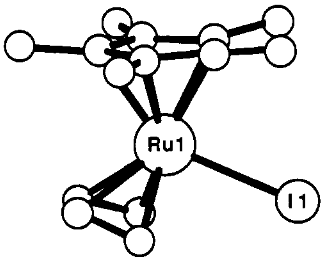
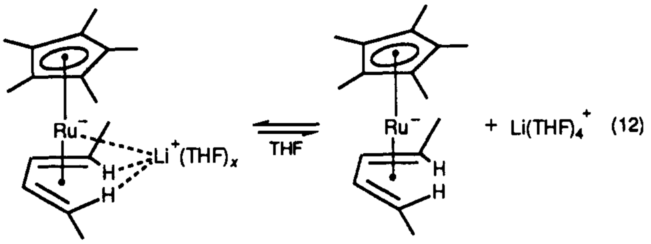


Figure 4. Alternative view of Cp*Ru(η^4-1,3-butadiene)I.

temperature in the ^{1}H NMR spectrum, two broad resonances assigned to the protons of the coordinated ethylene ligands were observed at δ −0.53 and 0.43. At −80 °C, each of the latter two resonances was split into two triplets; the two triplets that coalesced to the δ −0.53 resonance appeared at δ −0.82 (J = 9 Hz) and −0.18 (J = 9 Hz), and the other two triplets, which coalesced to the δ 0.43 resonance, appear at δ 0.54 (J = 9 Hz) and 0.33 (J = 9 Hz). The observation of these resonances as triplets rather than doublets of doublets suggest that the trans-vicinal $J^3{}_{HH}$ coupling constants are approximately equal to the cis-vicinal $J^3{}_{HH}$ coupling constants. Similarly, at −80 °C in the ^{13}C NMR spectrum, besides resonances assigned to the Cp* ligand, two separate triplets assigned to the coordinated ethylene ligands were observed at δ 18.1 and 31.3.

The ^{1}H NMR spectrum of the complex Cp*Ru(η^4-*trans*-2,*trans*-4-hexadiene)Li·DME dissolved in THF-d_8 had two separate sets of resonances (see Table III and the ^{13}C NMR data in Table IV), which we interpret as an ion-pairing phenomena due to the equilibrium shown in eq 12. In line with this interpretation, the intensity ratio of these two species at room temperature is concentration dependent; the intensity ratio of the diene proton resonance at δ −1.27 to that at δ −1.96 is 1.19 for a 0.075 M solution, whereas the corresponding ratio for a 0.034 M solution is 0.74. In this case, the rates of the equilibrium are slow enough on the NMR time scale and the equilibrium constant is favorable for observing both species in solution.



Conclusion

The complex 1 has proved to be a valuable synthetic precursor to a number of Ru(II) complexes and has allowed a synthetic entry to the anions Cp*Ru(η^4-diene)$^-$ and Cp*Ru(η^2-C$_2$H$_4$)$_2^-$. These anionic Ru(0) complexes can be protonated and alkylated to yield the corresponding hydride and alkyl derivatives, which undergo further alkyl and hydride migration reactions. This chemistry will be described in future contributions.

Experimental Section

All procedures were carried out in a glovebox equipped with a constant nitrogen flush or in Schlenk-type glassware interfaced to a high-vacuum (10^{-4}–10^{-5} Torr) line. Solvents were dried and distilled under dinitrogen before use by employing the following drying agents: Na dispersion or Na/benzophenone: tetra-

Table IV. ^{13}C NMR Data for $Cp^*Ru(\eta^4\text{-diene})Li \bullet DME$ Complexes[a,b]

compound	δ: Cp*	δ: diene	δ: DMA
$Cp^*Ru(\eta^4$-1,3-butadiene)Li·DME	12.7 (q, 124); 82.4 (s)	22.4 (t, 140); 68.6 (d, 161)	58.9 (q, 140); 72.7 (t, 139)
·$Cp^*Ru(\eta^4$-*trans*-1,3-pentadiene)Li·DME	12.5 (q, 124); 82.3 (s)	21.5 (q, 122); 22.2 (t, 142); 30.6 (d, 143); 67.4 (d, 160); 74.7 (d, 156)	58.9 (q, 140); 72.7 (t, 140)
·$Cp^*Ru(\eta^4$-*trans*-2,*trans*-4-hexadiene)Li·DME[c]	12.6 (q, 124);[d] 82.6 (s);[d] 12.7 (q, 125); 82.3 (s)	21.9 (q, 122);[d] 31.4 (d, 141);[d] 74.4 (d, 157)[d] 22.5 (q, 121); 29.5 (d, 145); 74.3 (d, 160)	58.9 (q, 140); 72.7 (t, 142)
$Cp^*Ru(\eta^4$-2,3-dimethyl-1,3-butadiene)Li·DME	12.4 (q, 124); 81.7 (s)	20.7 (q, 124, CH_3); 28.4 (t, 142, $=CH_2$); 74.2 (s, $C=CH_2$)	58.9 (q, 141); 72.7 (t, 140)
·$Cp^*Ru(\eta^4$-2,3-diphenyl-1,3-butadiene)Li·DME	12.0 (q, 125); 81.2 (s)	31.1 (t, 142); 83.5 (s); 123.3 (d, 158); 126.9 (d, 156); 131.2 (d, 158); 148.7 (s)	58.9 (q, 141); 72.7 (t, 140)
$Cp^*Ru(\eta^4$-1,3-cyclohexadiene)Li·DME	12.8 (q, 124); 81.5 (s)	29.0 (t, 123, CH_2); 40.8 (d, 143); 69.6 (d, 161)	58.9 (q, 140); 72.7 (t, 139)
$Cp^*Ru(\eta^4$-1,3-cycloheptadiene)Li·DME	13.0 (q, 124); 81.2 (q, 132)	30.0 (t, 117); 31.3 (t, 128); 39.7 (d, 141); 71.1 (d, 154)	58.9 (q, 140); 72.7 (t, 141)
$Cp^*Ru(\eta^4$-1,5-cyclooctadiene)Li·DME	11.2 (q, 124); 86.0 (s)	35.5 (t, 122, CH_2); 52.9 (d, 147, $CH=CH$)	58.9 (q, 140); 72.6 (t, 140)
$Cp^*Ru(\eta^4$-2,5-norbornadiene)Li·DME	12.2 (q, 124); 85.5 (s)	15.9 (d, 163, $CH=CH$); 51.6 (d, 137, CH); 55.9 (t, 128, CH_2)	58.9 (d, 140); 72.7 (t, 139)

[a] Reported in ppm from tetramethylsilane (75.5 MHz at 25 °C) in THF-d_8 unless indicated otherwise (s = singlet, d = doublet, t = triplet, q = quartet); numbers in parentheses are C–H coupling constants (hertz) unless otherwise specified. Other small two-bond $^{13}C-C-^{1}H$ couplings (<8 Hz) observed for some of the resonances are not reported. [b] Data were obtained from ^1H-decoupled and ^1H gated decoupled spectra. [c] Equilibrium mixture of two species. Data obtained from a 0.075 M solution. [d] Major species at this concentration.

Table V. Interatomic Distances for $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ (Å)[a]

bond	distance	bond	distance
Ru1–Cl1	2.514 (3)	C12–C13	1.408 (15)
Ru1–Cl3	2.536 (3)	C12–C17	1.482 (17)
Ru1–Cl4	2.520 (3)	C13–C14	1.414 (15)
Ru2–Cl1	2.521 (3)	C13–C18	1.478 (15)
Ru2–Cl2	2.533 (3)	C14–C19	1.491 (15)
Ru2–Cl3	2.521 (3)	C20–C21	1.443 (16)
Ru3–Cl1	2.513 (3)	C20–C24	1.444 (16)
Ru3–Cl2	2.531 (3)	C20–C25	1.481 (17)
Ru3–Cl4	2.526 (3)	C21–C22	1.405 (16)
Ru4–Cl2	2.513 (3)	C21–C26	1.459 (16)
Ru4–Cl3	2.537 (3)	C22–C23	1.390 (16)
Ru4–Cl4	2.528 (3)	C22–C27	1.510 (17)
Ru1–C10	2.088 (10)	C23–C24	1.410 (16)
Ru1–C11	2.104 (10)	C23–C28	1.515 (16)
Ru1–C12	2.098 (11)	C24–C29	1.483 (17)
Ru1–C13	2.096 (11)	C30–C31	1.426 (17)
Ru1–C14	2.106 (10)	C30–C34	1.414 (15)
Ru2–C20	2.101 (10)	C30–C35	1.512 (18)
Ru2–C21	2.112 (10)	C31–C32	1.396 (16)
Ru2–C22	2.096 (10)	C31–C36	1.497 (16)
Ru2–C23	2.083 (10)	C32–C33	1.413 (14)
Ru2–C24	2.106 (10)	C32–C37	1.517 (17)
Ru3–C30	2.068 (11)	C33–C34	1.417 (15)
Ru3–C31	2.098 (10)	C33–C38	1.495 (16)
Ru3–C32	2.100 (11)	C34–C39	1.478 (16)
Ru3–C33	2.103 (11)	C40–C41	1.354 (18)
Ru3–C34	2.111 (9)	C40–C44	1.401 (19)
Ru4–C40	2.094 (11)	C40–C45	1.527 (19)
Ru4–C41	2.110 (12)	C41–C42	1.389 (19)
Ru4–C42	2.081 (13)	C41–C46	1.519 (18)
Ru4–C43	2.110 (12)	C42–C43	1.351 (18)
Ru4–C44	2.092 (12)	C42–C47	1.482 (20)
C10–C11	1.454 (15)	C43–C44	1.480 (20)
C10–C14	1.421 (14)	C43–C48	1.458 (20)
C10–C15	1.479 (16)	C44–C49	1.411 (18)
C11–C12	1.407 (16)		
C11–C16	1.484 (15)		

[a] Numbers in parentheses are estimated standard deviations in the least significant figure.

Table VI. Intramolecular Angles for $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ (deg)[a]

atoms	angle	atoms	angle
Cl1–Ru1–Cl3	82.07 (9)	C20–C21–C22	107 (1)
Cl1–Ru1–Cl4	81.65 (9)	C20–C21–C26	127 (1)
Cl3–Ru1–Cl4	82.10 (9)	C22–C21–C26	126 (1)
Cl1–Ru2–Cl2	81.86 (8)	C21–C22–C23	110 (1)
Cl1–Ru2–Cl3	82.24 (8)	C21–C22–C27	124 (1)
Cl2–Ru2–Cl3	81.31 (9)	C23–C22–C27	126 (1)
Cl1–Ru3–Cl2	82.07 (8)	C22–C23–C24	109 (1)
Cl1–Ru3–Cl4	81.53 (8)	C22–C23–C28	126 (1)
Cl2–Ru3–Cl4	82.37 (8)	C24–C23–C28	125 (1)
Cl2–Ru4–Cl3	81.38 (9)	C20–C24–C23	107 (1)
Cl2–Ru4–Cl4	82.67 (8)	C20–C24–C29	125 (1)
Cl3–Ru4–Cl4	81.93 (9)	C23–C24–C29	128 (1)
Ru1–Cl1–Ru2	97.45 (9)	C31–C30–C34	109 (1)
Ru1–Cl1–Ru3	98.25 (9)	C31–C30–C35	125 (1)
Ru2–Cl1–Ru3	97.83 (10)	C34–C30–C35	126 (1)
Ru2–Cl2–Ru3	97.06 (9)	C30–C31–C32	107 (1)
Ru2–Cl2–Ru4	98.43 (9)	C30–C31–C36	127 (1)
Ru3–Cl2–Ru4	96.95 (9)	C32–C31–C36	126 (1)
Ru1–Cl3–Ru2	96.88 (9)	C31–C32–C33	109 (1)
Ru1–Cl3–Ru4	97.15 (9)	C31–C32–C37	126 (1)
Ru2–Cl3–Ru4	98.13 (9)	C33–C32–C37	125 (1)
Ru1–Cl4–Ru3	97.74 (9)	C32–C33–C34	108 (1)
Ru1–Cl4–Ru4	97.79 (9)	C32–C33–C38	127 (1)
Ru3–Cl4–Ru4	96.68 (9)	C34–C33–C38	125 (1)
C11–C10–C14	108 (1)	C30–C34–C33	107 (1)
C11–C10–C15	127 (1)	C30–C34–C39	127 (1)
C14–C10–C15	126 (1)	C33–C34–C39	126 (1)
C10–C11–C12	107 (1)	C41–C40–C44	110 (1)
C10–C11–C16	126 (1)	C41–C40–C45	124 (2)
C12–C11–C16	127 (1)	C44–C40–C45	125 (2)
C11–C12–C13	109 (1)	C40–C41–C42	108 (1)
C11–C12–C17	124 (1)	C40–C41–C46	127 (2)
C13–C12–C17	127 (1)	C42–C41–C46	125 (2)
C12–C13–C14	109 (1)	C41–C42–C43	110 (1)
C12–C13–C18	125 (1)	C41–C42–C47	125 (2)
C14–C13–C18	127 (1)	C43–C42–C47	124 (2)
C10–C14–C13	108 (1)	C42–C43–C44	107 (1)
C10–C14–C19	126 (1)	C42–C43–C48	130 (2)
C13–C14–C19	127 (1)	C44–C43–C48	123 (2)
C21–C20–C24	108 (1)	C40–C44–C43	105 (1)
C21–C20–C25	126 (1)	C40–C44–C49	129 (2)
C24–C20–C25	126 (1)	C43–C44–C49	126 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant figure.

hydrofuran (THF), 1,2-dimethoxyethane (DME), diethyl ether, and hexane (note: complex 1 will react with benzene contaminating diethyl ether, DME, or THF distilled from Na/benzophenone; therefore solutions of 1 were handled exclusively in diethyl ether, hexane, DME, or THF that were distilled from Na dispersion under N_2); CaH_2: CH_2Cl_2. Deuterated NMR solvents were dried similarily and were vacuum transferred into storage vessels. Complex 1 was prepared as described in detail elsewhere.[1]

Table VII. Interatomic Distances for Cp*Ru(η-1,3-butadiene)I (Å)[a]

bond	length	bond	length
I1–Ru1	2.7342 (4)	C3–C4	1.401 (5)
Ru1–C1	2.217 (3)	C5–C6	1.439 (3)
Ru1–C2	2.152 (3)	C5–C9	1.436 (4)
Ru1–C3	2.158 (3)	C5–C50	1.492 (4)
Ru1–C4	2.228 (3)	C6–C7	1.410 (4)
Ru1–C5	2.203 (2)	C6–C60	1.494 (4)
Ru1–C6	2.224 (3)	C7–C8	1.452 (4)
Ru1–C7	2.223 (3)	C7–C70	1.502 (4)
Ru1–C8	2.227 (3)	C8–C9	1.420 (4)
Ru1–C9	2.219 (2)	C8–C80	1.489 (4)
C1–C2	1.408 (5)	C9–C90	1.500 (4)
C2–C3	1.430 (5)		

[a] Numbers in parentheses are estimated standard deviations in the least significant figure.

Table VIII. Intramolecular Angles for Cp*Ru(η-1,3-butadiene)I (deg)[a]

atoms	angle	atoms	angle
I1–Ru1–C1	84.4 (1)	Ru1–C5–C9	71.7 (1)
I1–Ru1–C2	117.4 (1)	Ru1–C5–C50	128.6 (2)
I1–Ru1–C3	116.74 (8)	Ru1–C6–C5	70.2 (1)
I1–Ru1–C4	83.73 (9)	Ru1–C6–C7	71.5 (1)
I1–Ru1–C5	149.29 (7)	Ru1–C6–C60	126.0 (2)
I1–Ru1–C6	120.95 (7)	Ru1–C7–C6	71.6 (1)
I1–Ru1–C7	88.50 (7)	Ru1–C7–C8	71.1 (1)
I1–Ru1–C8	88.33 (7)	Ru1–C7–C70	129.7 (2)
I1–Ru1–C9	121.02 (7)	Ru1–C8–C7	70.8 (1)
C1–Ru1–C2	37.6 (1)	Ru1–C8–C9	71.0 (1)
C1–Ru1–C3	68.3 (1)	Ru1–C8–C80	129.1 (2)
C1–Ru1–C4	79.5 (1)	Ru1–C9–C5	70.4 (1)
C1–Ru1–C5	118.2 (1)	Ru1–C9–C8	71.7 (1)
C1–Ru1–C6	103.3 (1)	Ru1–C9–C90	125.1 (2)
C1–Ru1–C7	120.4 (1)	C1–C2–C3	119.9 (3)
C1–Ru1–C8	157.7 (1)	C2–C3–C4	120.4 (3)
C1–Ru1–C9	154.5 (1)	C6–C5–C9	108.3 (2)
C2–Ru1–C3	38.8 (1)	C6–C5–C50	125.4 (2)
C2–Ru1–C4	68.2 (1)	C9–C5–C50	125.8 (2)
C2–Ru1–C5	91.5 (1)	C5–C6–C7	107.7 (2)
C2–Ru1–C6	98.7 (1)	C5–C6–C60	125.6 (2)
C2–Ru1–C7	133.2 (1)	C7–C6–C60	126.7 (2)
C7–Ru1–C9	62.9 (1)	C6–C7–C8	108.5 (2)
C8–Ru1–C9	37.3 (1)	C6–C7–C70	125.8 (2)
Ru1–C1–C2	68.7 (2)	C8–C7–C70	125.2 (2)
Ru1–C2–C1	73.8 (2)	C7–C8–C9	107.7 (2)
Ru1–C2–C3	70.8 (2)	C7–C8–C80	125.3 (3)
Ru1–C3–C2	70.4 (2)	C9–C8–C80	126.6 (3)
Ru1–C3–C4	74.1 (2)	C5–C9–C8	107.8 (2)
Ru1–C4–C3	68.7 (2)	C5–C9–C90	125.4 (2)
Ru1–C5–C6	71.8 (1)	C8–C9–C90	126.8 (3)

[a] Numbers in parentheses are estimated standard deviations in the least significant figure.

Reagents used in this study that were purchased from commercial sources and used without further purification were as follows: 1,3-pentadiene, *trans*-2,*trans*-4-hexadiene, 2,3-dimethyl-1,3-butadiene, 1,3-cyclohexadiene, 1,3-cycloheptadiene, 1,5-cyclooctadiene, norbornadiene, and 1 M triethylborohydride in THF (Aldrich); 2,3-diphenyl-1,3-butadiene (Fluka); ethylene (Matheson, C.P.), 1,3-butadiene (Matheson) and CO (99.95%, Matheson); ethyllithium (Organometallics). Lithium powder was purchased as a paraffin wax dispersion (Alfa), stirred in hexane to dissolve the wax, isolated by filtration, and dried in vacuo. **CAUTION**: The latter procedure should be carried out under an argon atmosphere as the lithium powder prepared in this way can ignite spontaneously at room temperature under a nitrogen atmosphere forming lithium nitride. The lithium powder should be handled only under an argon atmosphere! Elemental analyses were performed by Oneida Research Services, Inc.

$Cp^*Ru(CO)_2Cl$. A 100-mL flask was charged with 1.00 g (0.920 mmol) of 1 and 30 mL of THF. Carbon monoxide was bubbled slowly through the solution over 40 min, and the solution was then stirred for an additional 20 min under the CO atmosphere. The solution was filtered, and THF was removed in vacuo. The light orange–yellow residue was triturated with 5 mL of hexane. The insoluble solid was collected by filtration, washed twice with 2-mL portions of hexane, and dried in vacuo to yield 1.05 g (87%) of $Cp^*Ru(CO)_2Cl$. IR (THF) 2028 (s), 1974 (s) cm^{-1}. ^1H NMR (THF-d_8) δ 1.90.

$Cp^*Ru[P(CH_3)_3]_2Cl$. A 25-mL flask was charged with 0.500 g (0.460 mmol) of 1, 10 mL of THF, and 400 μL of trimethylphosphine. After stirring for 10 min, the solution was filtered and solvent was removed in vacuo. Hexane (10 mL) was added to the flask, and this was cooled to −78 °C. The orange solid was collected by cold filtration and dried in vacuo, yield 0.414 g (53%). ^1H NMR (THF-d_8, 25 °C, 300 MHz) δ 1.38 (m, 18 H, PMe_3), 1.63 (t, 15 H, J_{HP} = 1.4 Hz, Cp*). ^{13}C NMR (THF-d_8, 25 °C, 75.5 MHz) δ 11.1 (q, J_{CH} = 126 Hz, Cp*), 20.6 (qt, J_{CH} = 126 Hz, J_{CP} = 13 Hz, PMe_3), 88.2 (s, Cp*). Anal. Calcd for $C_{16}H_{33}ClP_2Ru$: C, 45.33; H, 7.85; Cl, 8.36; P, 14.61. Found: C, 45.37; H, 7.70; Cl, 7.18; P, 14.33.

$Cp^*Ru(CO)_2H$. A 100-mL flask was charged with 0.800 g (2.94 mmol) of 1 and 20 mL of THF. On a high-vacuum line, an atmosphere of CO was admitted to the flask, and CO uptake was monitored with a mercury manometer. After CO uptake was complete, solvents and excess CO were removed in vacuo. Diethyl ether (40 mL) was then added to the flask under a nitrogen atmosphere, and 3.0 mL of 1.0 M lithium triethylborohydride (3.0 mmol) was added to the flask at room temperature. After stirring for 10 min, solvent was removed in vacuo. Chromatography of the residue on activity III alumina using first diethyl ether and then THF as elutants yielded fractions containing the product. Removal of solvent from these fractions followed by sublimation (50 °C, 10^{-4} Torr) yielded 0.585 g (68%) of $Cp^*Ru(CO)_2H$ as a colorless crystalline solid.

$Cp^*Ru(\eta^3\text{-}C_3H_5)Cl_2$. A 25-mL flask was charged with 0.500 g (0.460 mmol) of 1 and 10 mL of THF. Upon addition of 200 μL (2.45 mmol) of 3-chloropropene, an immediate reaction occurred, and an orange precipitate formed. After this was stirred for another 10 min, 12 mL of hexane was added to the reaction, and the crystalline orange solid was collected by filtration, was washed once with 2 mL of hexane, and was dried to yield 0.604 g of product. This was recrystallized by dissolving in 15 mL of CH_2Cl_2, filtering the solution, and precipitating the product with 75 mL of hexane. The orange crystals were collected by filtration and dried in vacuo, yield 0.557 g (86%). ^1H NMR (THF-d_8, 25 °C, 300 MHz) δ 1.59 (s, 15 H, Cp*), 2.42 (d, 2 H, J = 9.8 Hz, allyl), 3.87 (d, 2 H, J = 6.0 Hz, allyl), 4.93 (m, 1 H, allyl). ^{13}C NMR (CD_2Cl_2, 25 °C, 75.5 MHz) δ 9.76 (q, J_CH = 129 Hz, Cp*), 68.1 (t, J_{CH} = 162 Hz, allyl), 97.7 (d, J_{CH} = 174 Hz, allyl), 105.1 (s, Cp*). Anal. Calcd for $C_{13}H_{20}Cl_2Ru$: C, 44.83; H, 5.79; Cl, 20.36. Found: C, 44.75; H, 5.59; Cl, 19.33.

$[Cp^*Ru(\eta^2\text{-}C_2H_4)Cl]_x$. A quartz Fischer-Porter thick-walled pressure vessel was charged with 5.00 g (4.60 mmol) of 1, and 20 mL of DME was added. After attachment of the pressure head, the vessel was placed behind a safety shield, and the atmosphere was replaced with 60 psi of ethylene. This pressure was maintained throughout the course of the reaction. After 23 h, the ethylene was vented, and the apparatus was transferred into a glovebox. After addition of 20 mL of hexane to the vessel, the red solid was collected by filtration, washed with 10 mL of hexane, and dried by pulling nitrogen through the filter cake, yield 5.24 g (95%). By ^1H NMR in THF-d_8, this solid contains an approximately 2:1 mole ratio of $[Cp^*Ru(\eta^2\text{-}C_2H_4)Cl]_x$:1. ^1H NMR (THF-d_8, 300 MHz, 25 °C) δ 1.33 (s, 15 H, Cp*), 3.87 (br s, 4 H, $\eta^2\text{-}C_2H_4$), 1.56 (s, Cp* of 1).

$[Cp^*Ru(\mu_3\text{-}I)]_4$. A 50-mL round-bottomed flask was charged with 1.00 g (0.920 mmol) of 1, and 30 mL of CH_3CN was added. This was refluxed until all of the $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ had dissolved, and the solution was then cooled to room temperature. Sodium iodide (0.552 g, 3.68 mmol) was added to the reaction flask. After stirring for 30 min, the solution was filtered, and solvent was removed in vacuo. Diethyl ether (20 mL) was added to the residue, and the orange–red solid collected by filtration. The solid was washed twice with 2-mL portions of diethyl ether and dried in vacuo, yield 1.22 g (91%). ^1H NMR (THF-d_8, 300 MHz, 25 °C) δ 1.69 (s, Cp*). Anal. Calcd for $C_{40}H_{60}I_4Ru_4$: C, 33.07; H, 4.16. Found: C, 33.51; H, 4.25.

$Cp^*Ru(\eta^4\text{-}1,3\text{-butadiene})I$. A 100-mL flask was charged with 0.400 g (0.275 mmol) of $[Cp^*Ru(\mu_3\text{-}I)]_4$ and 30 mL of THF were added to the flask. The mixture was stirred, 1,3-butadiene gas was bubbled slowly through the solution for ca. 20 min, and the solution was then stirred under the atmosphere of 1,3-butadiene for an additional 10 min. The solution was then filtered, and solvent was removed in vacuo. Hexane (10 mL) was added to the solid residue, and the orange solid was collected by filtration, washed twice with 1-mL portions of hexane, and dried in vacuo, yield 0.357 g (78%). Anal. Calcd for $C_{14}H_{21}IRu$: C, 40.30; H, 5.07. Found: C, 40.56; H, 4.95.

Cp*Ru(η^4-1,3-butadiene)Cl. A 100-mL round-bottomed flask was charged with 1.00 g (0.920 mmol) of 1, and 40 mL of THF was added. After 1,3-butadiene gas was bubbled through the solution for 20 min, the mixture was stirred for an additional 30 min under the 1,3-butadiene atmosphere. The solution was then filtered, and solvent was removed from the filtrate in vacuo. Hexane (10 mL) was added to the solid residue, and the orange insoluble solid was collected by filtration, washed twice with 0.5-mL portions of hexane, and dried in vacuo, yield 1.06 g (88%). Anal. Calcd for $C_{14}H_{21}ClRu$: C, 51.61; H, 6.50. Found: C, 51.72; H, 6.40.

Cp*Ru(η^4-*trans*-1,3-pentadiene)Cl. A 50-mL round-bottomed flask was charged with 0.600 g (0.552 mmol) of 1, and 20 mL of THF was added. Then, 250 μL (2.51 mmol) of 1,3-pentadiene was added to the flask, and the reaction was stirred for 30 min. The solution was then filtered, and solvent was removed from the filtrate in vacuo. Hexane (5 mL) was added to the solid residue, and the orange insoluble solid was collected by filtration, washed twice with 0.5-mL portions of hexane, and dried in vacuo, yield 0.737 g (79%). Anal. Calcd for $C_{15}H_{23}ClRu$: C, 53.01; H, 6.82. Found: C, 52.90; H, 6.71.

Cp*Ru(η^4-*trans*-2,*trans*-4-hexadiene)Cl. A 50-mL round-bottomed flask was charged with 0.600 g (0.552 mmol) of 1, and 20 mL of THF was added. Then, 290 μL (2.54 mmol) of *trans*-2,*trans*-4-hexadiene was added to the flask, and the reaction was stirred for 30 min. The solution was filtered, and solvent was removed from the filtrate in vacuo. Hexane (10 mL) was added to the solid residue, and the orange insoluble solid was collected by filtration, washed twice with 2-mL portions of hexane, and dried in vacuo, yield 0.750 g (96%). Anal. Calcd for $C_{16}H_{25}ClRu$: C, 54.30; H, 7.12. Found: C, 54.19; H, 7.19.

Cp*Ru(η^4-2,3-dimethyl-1,3-butadiene)Cl. A 50-mL round-bottomed flask was charged with 0.500 g (0.460 mmol) of 1 and 40 mL of THF. Then, 250 μL (2.21 mmol) of 2,3-dimethyl-1,3-butadiene was added to the flask, and the reaction was stirred for 40 min. The solution was then filtered, and solvent was removed from the filtrate in vacuo. Hexane (5 mL) was added to the solid residue, and the orange insoluble solid was collected by filtration, washed twice with 0.5-mL portions of hexane, and dried in vacuo, yield 0.571 g (88%). Anal. Calcd for $C_{16}H_{25}ClRu$: C, 54.30; H, 7.12. Found: C, 54.25; H, 6.98.

Cp*Ru(*s*-*cis*-η^4-2,3-diphenyl-1,3-butadiene)Cl and Cp*Ru(*s*-*trans*-η^4-2,3-diphenyl-1,3-butadiene)Cl. A 50-mL round-bottomed flask was charged with 2.00 g (1.84 mmol) of 1, 40 mL of diethyl ether, and 2.00 mL of 2,3-diphenyl-1,3-butadiene. This was stirred for 40 min, at which time a precipitate was observed in the flask. The solution was filtered, and the filter cake was extracted with a total of 250 mL of diethyl ether. The remaining solid on the frit was dried in vacuo and amounted to 1.48 g; this was retained. The filtrate was concentrated in vacuo to ca. 20 mL, and then 40 mL of hexane was added. The solid that formed was collected by filtration, washed twice with 2-mL portions of hexane, and dried in vacuo to yield 1.01 g of a beige solid which was the desired product. The 1.48 g of solid retained above was extracted with three 70-mL portions of 2:1 diethyl ether/THF, and these extracts were filtered and combined. Solvent was removed from the filtrate in vacuo. Hexane (80 mL) was added to the residue, and the solid was collected by filtration, washed twice with 2-mL portions of hexane, and dried in vacuo to yield 0.747 g of product. Total yield was thus 1.76 g (50%). Because of the instability of this complex, no further purification was attempted, and the product was used in further experiments as obtained. Anal. Calcd for $C_{26}H_{29}ClRu$: C, 65.33; H, 6.11; Cl, 7.42. Found: C, 64.80; H, 6.18; Cl, 5.85.

Cp*Ru(η^4-1,3-cyclohexadiene)Cl. A 100-mL round-bottomed flask was charged with 6.04 g (5.55 mmol) of 1, and 70 mL of THF was added. While this was stirring, 2.7 mL (28 mmol) of 1,3-cyclohexadiene was added to the flask, and the reaction was allowed to proceed for 50 min, at which time the solution was filtered. Solvent was removed from the filtrate in vacuo, and 30 mL of hexane was added to the residue. After trituration, the orange solid was collected by filtration, washed twice with 3-mL portions of hexane, and dried in vacuo, yield 7.30 g (93%). Anal. Calcd for $C_{16}H_{23}ClRu$: C, 54.61; H, 6.59. Found: C, 54.50; H, 6.69.

Cp*Ru(η^4-1,3-cycloheptadiene)Cl. A 50-mL round-bottomed flask was charged with 0.800 g (0.734 mmol) of 1 and 20 mL of THF. While this was stirring, 350 μL (3.23 mmol) of 1,3-cycloheptadiene was added to the flask, and the reaction was allowed to proceed for 30 min at which time the solution was filtered. Solvent was removed from the filtrate in vacuo, and 10 mL of hexane was added to the residue. After trituration, the orange solid was collected by filtration, washed twice with 3-mL portions of hexane, and dried in vacuo, yield 0.875 g (81%). Anal. Calcd for $C_{17}H_{25}ClRu$: C, 55.80; H, 6.89. Found: C, 55.71; H, 6.83.

Cp*Ru(η^4-1,5-cyclooctadiene)Cl. A 25-mL round-bottomed flask was charged with 0.500 g (0.460 mmol) of 1, 10 mL of THF, and 300 μL (2.45 mmol) of 1,5-cyclooctadiene. After stirring for 1 h, the solution was filtered, and solvent was removed in vacuo. Hexane (5 mL) was added to the residue, and after trituration of the yellow–orange solid it was collected by filtration, washed twice with 2-mL portions of hexane, and dried in vacuo, yield 0.658 g (94%). Anal. Calcd for $C_{18}H_{27}ClRu$: C, 56.90; H, 7.16. Found: C, 57.03; H, 7.23.

Cp*Ru(η^4-2,5-norbornadiene)Cl. A 200-mL round-bottomed flask was charged with 2.00 g (1.84 mmol) of 1, 80 mL of THF, and 1.00 mL (9.27 mmol) of 2,5-norbornadiene. After stirring for 20 min, the solution was filtered, and solvent was removed in vacuo. Hexane (20 mL) was added to the residue, and after trituration the yellow–orange solid was collected by filtration, washed once with 2 mL of hexane, and dried in vacuo, yield 2.52 g (94%). Anal. Calcd for $C_{17}H_{23}ClRu$: C, 56.11; H, 6.37. Found: C, 56.22; H, 6.36.

Cp*Ru(η^2-C_2H_4)$_2$Li. A 200-mL flask with a stopcock/sidearm that had a septum attached was charged with 5.24 g of [Cp*Ru(η^2-C_2H_4)Cl]$_x$. On a high-vacuum line, the flask was cooled to −78 °C and was then evacuated. A total of 75 mL of DME was vacuum transferred into the flask. An atmosphere of ethylene was admitted to the flask, and after the stopcock was opened, 33.6 mL of a 1.04 M solution of ethyllithium in benzene was added through the septum via syringe. The stopcock was then closed, and after the mixture stirred at −78 °C for 5 min, the dry ice–acetone bath was removed, and the mixture was allowed to warm to room temperature. As the mixture warms, the solids go into solution and gas is evolved from the solution. After stirring for 45 min, a white precipitate was observed in the flask, and the ethylene atmosphere and solvents were removed in vacuo. The solid residue was extracted twice with 60-mL portions of 1:1 (v:v) DME/diethyl ether, and each of these was filtered and solvent was removed from filtrate in vacuo. Then, 15 mL of toluene was added to the solid residue, and the white solid was collected by filtration. The solid was washed with 15 mL of toluene and twice with 5-mL portions of hexane. It was then dried in vacuo to yield 1.34 g. An equal volume of hexane was added to the toluene filtrate which had been combined with the toluene and hexane washings. The resulting white precipitate was collected by filtration, washed with hexane, and dried in vacuo to yield 1.64 g of product. The total yield of Cp*Ru(η^2-C_2H_4)$_2$Li was thus 2.98 g (ca. 58%). The product as obtained usually contained from 0.1 to 0.2 mol fraction of DME of coordination by ^{1}H NMR. Most of this could be removed by warming the solid under high vacuum. ^{1}H NMR (THF-d_8, 25 °C, 300 MHz) δ 1.62 (s, 15 H), 0.43 (br, 4 H), −0.53 (br, 4 H). ^{13}C NMR (THF-d_8, −80 °C, 75.5 MHz) δ 11.0 (q, J_{CH} = 121 Hz, Cp*), 18.1 (t, J_{CH} = 141 Hz, C_2H_4), 31.3 (t, J_{CH} = 147 Hz, C_2H_4), 87.1 (s, Cp*).

Cp*Ru(η^4-1,3-butadiene)Li·DME. A 100-mL round-bottomed flask was charged with 2.00 g (6.14 mmol) of Cp*Ru(η^4-1,3-butadiene)Cl and 0.250 g (36.0 mmol) of Li powder. The flask was evacuated, and 50 mL of DME was vacuum transferred into the flask at −50 °C (cyclohexanone–dry ice bath). After stirring for 1 h, the mixture was allowed to warm to 0 °C (ice bath) and was stirred for 10 min. Solvent was then removed in vacuo. The residue was extracted with four 20-mL portions of 1:1 (v/v) diethyl ether–DME, and these extracts were filtered and combined. Solvent was removed from the filtrate in vacuo. Diethyl ether (8 mL) was added to the residue, and the white solid was collected by filtration, washed twice with 0.5 mL of diethyl ether, and dried in vacuo, yield 1.45 g (61%).

Cp*Ru(η^4-1,3-pentadiene)Li·DME. A 50-mL round-bottomed flask was charged with 0.600 g (1.77 mmol) of Cp*Ru(η^4-1,3-pentadiene)Cl and 0.060 g (8.6 mmol) of Li powder. On a high-vacuum line, 20 mL of DME was vacuum transferred into the flask which was cooled with a −50 °C (dry ice–cyclohexanone) bath. The solution was stirred for 1 h and was then allowed to warm to 0 °C, whereupon the solution was stirred for 15 min. Solvent was then removed in vacuo. In a glovebox, the solid residue was extracted three times with 20-mL portions of 3:1 (v/v) DME–diethyl ether, each of which was filtered. Solvents were removed from the combined extracts in vacuo. A minimum of diethyl ether was added to the residue, and after trituration the white solid was collected by filtration, washed once with 0.5 mL of diethyl ether, and dried in vacuo, yield 0.333 g (47%).

Cp*Ru(η^4-*trans*-2,*trans*-4-hexadiene)Li·DME. A 100-mL round-bottomed flask was charged with 0.730 g (2.06 mmol) of Cp*Ru(η^4-*trans*-2,*trans*-4-hexadiene)Cl and 0.200 g (28.8 mmol) of Li powder. The flask was evacuated, and 50 mL of DME was vacuum transferred into the flask at −50 °C (cyclohexanone–dry ice bath). After stirring for 1.5 h, the mixture was allowed to warm to 0 °C, and was then stirred at 0 °C (ice bath) for 15 min. Solvent was then removed in vacuo. The residue was extracted with three 20-mL portions of 1:1 (v/v) diethyl ether/DME, and these extracts were filtered and combined. Solvent was removed from the filtrate in vacuo. Diethyl ether (10 mL) was added to the residue, and the white solid was collected by filtration, washed with 5 mL of ether–hexane, and dried in vacuo, yield 0.210 g (25%).

Cp*Ru(η^4-2,3-dimethyl-1,3-butadiene)Li·DME. A 50-mL round-bottomed flask was charged with 1.54 g (4.35 mmol) of Cp*Ru(η^4-2,3-dimethyl-1,3-butadiene)Cl and 0.138 g (19.9 mmol) of Li powder. On a high-vacuum line, 30 mL of DME was vacuum transferred into the flask which was cooled with a −50 °C (dry ice–cyclohexanone) bath. The reaction mixture was stirred for 1 h and was then allowed to warm to 0 °C, whereupon the mixture was stirred for 20 min. Solvent was then removed in vacuo. In a glovebox, the solid residue was extracted four times with 20-mL portions of 1:1 (v/v) DME–diethyl ether, each of which was filtered. Solvents were removed from the combined extracts in vacuo. Diethyl ether (8 mL) was added to the residue, and after trituration the solid was collected by filtration, washed once with 2 mL of diethyl ether, and dried in vacuo to yield 1.41 g (78%) of a white solid.

Cp*Ru(η^4-2,3-diphenyl-1,3-butadiene)Li·DME. A 100-mL round-bottomed flask was charged with 0.638 g (1.33 mmol) of Cp*Ru(η^4-2,3-diphenyl-1,3-butadiene)Cl (mixture of isomers) and 0.210 g (30.3 mmol) of Li powder. The flask was evacuated, and 50 mL of DME was vaccum transferred into the flask at −50 °C (cyclohexanone–dry ice bath). After stirring for 1 h, the mixture was allowed to warm slowly to 0 °C over 30 min and was then stirred at 0 °C (ice bath) for 45 min. Solvent was then removed in vacuo. The residue was extracted with four 20-mL portions of 3:1 (v/v) diethyl ether–DME, and these extracts were filtered and combined. Solvent was removed from the filtrate in vacuo. Hexane (20 mL) was added to the residue, and the light yellow solid was collected by filtration, washed with 5 mL of hexane, and dried in vacuo, yield 0.606 g (84%).

Cp*Ru(η^4-1,3-cyclohexadiene)Li·DME. A 50-mL round-bottomed flask was charged with 2.366 g (6.724 mmol) of Cp*Ru(η^4-1,3-cyclohexadiene)Cl and 0.150 g (21.6 mmol) of Li powder. On a high-vacuum line, 20 mL of DME was vacuum transferred into the flask, which was cooled with a −78 °C dry ice–acetone bath. The orange solution was stirred for 1 h (warming to −60 °C if necessary in the event that the DME freezes) and was then allowed to warm to 0 °C, whereupon the solution was stirred for 20 min. Solvent was then removed in vacuo. In a glovebox, the solid residue was extracted three times with 20-mL portions of 1:1 (v/v) DME–diethyl ether, each of which was filtered. Solvents were removed from the combined extracts in vacuo. Diethyl ether (10 mL) was added to the residue, and after trituration the solid was collected by filtration, washed twice with 1-mL portions of diethyl ether, and dried in vacuo to yield 2.22 g (80%) of a light yellow solid. Anal. Calcd for $C_{20}H_{33}LiO_2Ru$: C, 58.10; H, 8.04; Li, 1.68. Found: C, 58.17; H, 7.85, Li, 1.70.

Cp*Ru(η^4-1,3-cycloheptadiene)Li·DME. A 50-mL round-bottomed flask was charged with 1.18 g (3.22 mmol) of Cp*Ru(η^4-1,3-cycloheptadiene)Cl and 0.212 g (30.5 mmol) of Li powder. On a high-vacuum line, 20 mL of DME was vacuum transferred into the flask, which was cooled with a −50 °C (dry ice–cyclohexanone) bath. The orange solution was stirred for 2.5 h and was then allowed to warm to 0 °C whereupon the solution was stirred for 20 min. Solvent was then removed in vacuo. In a glovebox, the solid residue was extracted three times with 20-mL portions of 1:1 (v/v) DME–diethyl ether, each of which was filtered. Solvents were removed from the combined extracts in vacuo. Hexane (10 mL) was added to the residue, and after trituration the solid was collected by filtration, washed twice with 1-mL portions of hexane, and dried in vacuo to yield 1.182 g (86%) of a white solid.

Cp*Ru(η^4-1,5-cyclooctadiene)Li·DME. A 100-mL round-bottomed flask was charged with 2.00 g (5.26 mmol) of Cp*Ru(η^4-1,5-cyclooctadiene)Cl and 0.200 g (28.8 mmol) of Li powder. The flask was evacuated, and 50 mL of DME was vacuum transferred into the flask at −50 °C (cyclohexanone–dry ice bath). After stirring for 1 h, the mixture was allowed to warm to 0 °C (ice bath) and was stirred for 15 min. Solvent was then removed in vacuo. The residue was extracted with four 20-mL portions of 1:1 (v/v) diethyl ether–DME, and these extracts were filtered and combined. Solvent was removed from the filtrate in vacuo. Diethyl ether (8 mL) was added to the residue, and the white solid was collected by filtration, washed twice with 0.5 mL of diethyl ether, and dried in vacuo, yield 1.71 g (74%).

Cp*Ru(η^4-norbornadiene)Li·DME. A 100-mL round-bottomed flask was charged with 2.41 g (6.62 mmol) of Cp*Ru(η^4-norbornadiene)Cl and 0.313 g (45.1 mmol) of Li powder. The flask was evacuated, and 50 mL of DME were vacuum transferred into the flask at −50 °C (cyclohexanone–dry ice bath). After stirring for 30 min, the mixture was allowed to warm to 0 °C (ice bath) and was stirred for 45 min. Solvent was then removed in vacuo. The residue was extracted with four 20-mL portions of 1:1 (v/v) diethyl ether–DME, and these extracts were filtered and combined. Solvent was removed from the filtrate in vacuo. A minimum of diethyl ether was added to the residue, and the light yellow solid was collected by filtration, washed with 2 mL of diethyl ether, and dried in vacuo, yield 2.30 g (82%).

X-ray Structural Analysis of [Cp*Ru(μ_3-Cl)]$_4$. A red–brown irregular block of 1 (ca. 0.15 × 0.25 × 0.25 mm) was grown by adding 1 equiv of lithium triethylborohydride to a THF solution of $(Cp^*RuCl_2)_x$ and allowing the solution to stand. The crystal was triclinic ($P\bar{1}$ (No. 2)) with the following cell dimensions determined from 20 reflections (μ(Mo) = 16.18 cm^{-1}): a = 11.281 (5); β = 11.354 (4); c = 18.846 (5) Å; α = 82.20 (2), β = 82.03 (3), γ = 65.45 (4)°; V = 2166.3 Å^3, Z = 2, FW = 1087.13 ($C_{40}H_{60}Cl_4Ru_4$), D_c = 1.666 g/cm^3.

Data were collected at −72 °C on an Enraf-Nonius CAD4 diffractometer with a graphite monochromator using Mo Kα radiation (λ = 0.7107 Å). A total of 10 258 data were collected with 2.2° ≤ 2θ ≤ 55.0° (maximum h,k,l = 14,14,24). The ω scan method was used with a scan width equal to 1.50–1.80° ω and a scan speed of 2.00–5.00°/min. Typical half-height peak widths were 0.49° ω. Three standards were collected 85 times, and data were adjusted for a 12% decrease in intensity and 13.0% variation in azimuthal scan. Data were corrected for absorption (DIFABS; range of transmission factors = 0.55–1.00; 164 duplicates, 1.9% R merge, 4748 unique reflections with $I \geq 3.0\ \sigma(I)$).

The structure was solved by automated Patterson analysis (PHASE) with refinement by full-matrix least-squares methods on F (scattering factors from ref 15) including anomolous terms for Ru and Cl, with weights $\alpha\ [\sigma^2(I) + 0.0009I^2]^{1/2}$. All non-hydrogen atoms were refined anisotropically (433 parameters), and H atom positions were fixed. The final R was 0.051 (R_w = 0.047) with an error of fit = 1.30 (maximum Δ/σ = 1.63). There was a high thermal motion about the Cp* rings. This may be a consequence of an observed temperature dependence of the crystal symmetry.

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(15) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4.

The crystal is apparently monoclinic at room temperature and undergoes a triclinic distortion at lower temperatures. The transformation to a monoclinic cell is $(110, 1\bar{1}0, 00\bar{1})$ and yields lattice parameters $a = 19.04$, $b = 12.24$, $c = 18.85$ Å; $\alpha = 90.11$, $\beta = 99.38$, $\gamma = 90.41°$. The crystal was cooled ca. 2 days before data collection. The largest residual density was 0.94 e/Å^3 near Ru4.

X-ray Structural Analysis of Cp*Ru(η^4-1,3-butadiene)I. A red irregular block (ca. 0.30 × 0.35 × 0.38 mm) was grown by gaseous diffusion of hexane into a THF solution. The crystal is monoclinic-*b* ($P2_1/c$ (No. 14)) with the following cell dimensions determined from 47 reflections (μ(Mo) = 32.13 cm^{-1}): $a = 7.177$ (2); $b = 14.362$ (3); $c = 13.788$ (2) Å; $\beta = 93.39$ (1)°; $V = 1418.7$ Å^3, $Z = 4$, FW = 417.32 ($C_{14}H_{21}IRu$), $D_c = 1.954$ g/cm^3.

Data were collected at −100 °C on a Syntex R3 diffractometer with a graphite monochromator using Mo Kα radiation. A total of 3673 data were collected with $4.1° \leq 2\theta \leq 55.0°$ (maximum h,k,l = 9,18,17, data octants = + + +, + + −). The ω-scan method was used with a scan width equal to 1.10° ω and a scan speed of 2.00–5.00°/min. Typical half-height peak widths were 0.25 ° ω. Three standards were collected 20 times with 2% fluctuation in intensity and 7.0% variation in azimuthal scan. Data were corrected for absorption (DIFABS; range of transmission factors = 0.26–0.36; 227 duplicates, 0.9% *R* merge, 2931 unique reflections with $I \geq 3.0\ \sigma(I)$).

The structure was solved by automated Patterson analysis (PHASE) with refinement by full-matrix least-squares methods on *F* (scattering factors from ref 15) including anomolous terms for Ru and I, with weights $\propto [\sigma^2(I) + 0.0009I^2]^{1/2}$. All non-hydrogen atoms were refined anisotropically (433 parameters), and H atom positions were located and refined isotropically. The final *R* was 0.020 ($R_w = 0.029$) with an error of fit = 1.53 (maximum Δ/σ = 0.15). The largest residual density was 0.39 e/Å^3 near Ru, Cl of the diene.

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Registry No. 1, 126821-58-7; Cp*Ru(CO)$_2$Cl, 77488-50-7; Cp*Ru[P(CH$_3$)$_3$]$_2$Cl, 87640-47-9; Cp*Ru(CO)$_2$H, 82728-97-0; Cp*Ru(η^3-C$_3$H$_5$)Cl$_2$, 126821-59-8; Cp*Ru(η^2-C$_2$H$_4$)Cl, 126821-60-1; [Cp*Ru(μ_3-I)]$_4$, 126847-86-7; Cp*Ru(η^4-1,3-butadiene)I, 126821-61-2; Cp*Ru(η^4-1,3-butadiene)Cl, 126821-62-3; Cp*Ru(η^4-*trans*-1,3-pentadiene)Cl, 126821-63-4; Cp*Ru(η^4-*trans*-2,*trans*-4-hexadiene)Cl, 126821-64-5; Cp*Ru(η^4-2,3-dimethyl-1,3-butadiene)Cl, 126821-65-6; Cp*Ru(*s-cis*-η^4-2,3-diphenyl-1,3-butadiene)Cl, 126821-66-7; Cp*Ru(*s-trans*-η^4-2,3-diphenyl-1,3-butadiene)Cl, 126923-01-1; Cp*Ru(η^4-1,3-cyclohexadiene)Cl, 126821-67-8; Cp*Ru(η^4-1,3-cycloheptadiene)Cl, 126821-68-9; Cp*Ru(η^4-1,5-cyclooctadiene)Cl, 92390-26-6; Cp*Ru(η^4-2,5-norbornadiene)Cl, 87640-46-8; Cp*Ru(η^2-C$_2$H$_4$)$_2$Li, 126821-69-0; Cp*Ru(η^4-1,3-butadiene)Li·DME, 126847-88-9; Cp*Ru(η^4-1,3-pentadiene)Li·DME, 126821-71-4; Cp*Ru(η^4-*trans*-2,*trans*-4-hexadiene)Li·DME, 126821-73-6; Cp*Ru(η^4-2,3-dimethyl-1,3-butadiene)Li·DME, 126821-75-8; Cp*Ru(η^4-2,3-diphenyl-1,3-butadiene)Li·DME, 126821-77-0; Cp*Ru(η^4-1,3-cyclohexadiene)Li·DME, 126821-79-2; Cp*Ru(η^4-1,3-cycloheptadiene)Li·DME, 126821-81-6; Cp*Ru(η^4-1,5-cyclooctadiene)Li·DME, 126821-83-8; Cp*Ru(η^4-norbornadiene)Li·DME, 126821-85-0; 3-chloropropene, 107-05-1; 1,3-butadiene, 106-99-0; 1,3-pentadiene, 504-60-9; *trans*-2,-*trans*-4-hexadiene, 5194-51-4; 2,3-dimethyl-1,3-butadiene, 513-81-5; 2,3-diphenyl-1,3-butadiene, 2548-47-2; 1,3-cyclohexadiene, 592-57-4; 1,3-cycloheptadiene, 4054-38-0; 1,5-cyclooctadiene, 111-78-4; 2,5-norbornadiene, 121-46-0.

Supplementary Material Available: X-ray data for 1 and Cp*Ru(η^4-1,3-butadiene)I, including tables of atomic positional parameters, thermal parameters, H atom fixed fractional coordinates, intra- and intermolecular nonbonding distances, and bond distances and bond angles involving H atoms (6 pages); a listing of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.