Reactions of [Cp*Ru(OMe)]2. 9. Olefin activation and formation of allyl complexes. Molecular structure of Cp*Ru(.eta.3-C3H5)(.eta.2-CH2:CHCH3)

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using the TEXSAN[22] crystallographic software package developed by Molecular Structure Corp.

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(22) *TEXSAN: Single Crystal Structure Analysis Software, Version 5.0*; Molecular Structure Corp.: The Woodlands, TX 77381, 1989.
(23) DIFABS: Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158. DIFABS defines the average transmission factor to be near unity; therefore, the minimum and maximum transmission factors will be less than and greater than unity, respectively.
(24) Least-squares function minimized: $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o)^2$, $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/(Lp)^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, Lp = Lorentz–polarization factor, and p = p factor.
(25) Standard deviation of an observation of unit weight: $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o = number of observations and N_v = number of variables.

Registry No. **1a**, 91410-27-4; **1b**, 111349-24-7; **1c**, 137466-31-0; **1d**, 94249-91-9; **1e**, 137466-32-1; **2a**, 137466-22-9; **2b**, 137466-24-1; **2c**, 137466-26-3; **2d**, 137466-28-5; **2e**, 137466-30-9; **2f**, 137494-31-6; **3**, 137466-34-3; **4**, 137466-36-5; **5a**, 137494-33-8; **5b**, 137466-38-7; **5c**, 137494-35-0; **5d**, 137466-40-1; **5e**, 137466-42-3; **5e-d**, 137466-50-3; **5f**, 137494-37-2; **6a**, 137466-44-5; **6b**, 137494-39-4; **6c**, 137466-46-7; **6f**, 137466-48-9; diphpyH_2, 3558-69-8; ditolpyH_2, 14435-88-2.

Supplementary Material Available: Tables of positional parameters and temperature factors, including the H atoms, full distances and bond angles, torsion or conformation angles, and anisotropic temperature factors (14 pages); a listing of structure factors (40 pages). Ordering information is given on any current masthead page.

Reactions of $[Cp^*Ru(OMe)]_2$. 9.[1] Olefin Activation and Formation of Allyl Complexes. Molecular Structure of $Cp^*Ru(\eta^3\text{-}C_3H_5)(\eta^2\text{-}CH_2{=}CHCH_3)$

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Simple olefin addition products of $[Cp^*Ru(OMe)]_2$ (1) are unstable at ambient temperature. Under slightly more forcing conditions the allyl complexes $Cp^*Ru(C_3H_4Me)(C_2H_4)$ (3) and $Cp^*Ru(C_3H_5)(C_2H_3Me)$ (4) are formed with ethylene and propylene, respectively. 4 crystallizes in the space group *Pbca* with a = 13.752 (3) Å, b = 14.576 (2) Å, c = 15.174 (4) Å, and Z = 8; R (R_w) = 0.027 (0.035) for 1837 independent reflections with $I > 3\sigma(I)$. Reaction of 1 with cyclic polyolefins proceeds with hydrogenation or dehydrogenation of the ligand to give $Cp^*Ru(\pi\text{-olefin})$ complexes.

Activation of olefins for oligomerization and polymerization at transition-metal centers still offers much attraction. Generally a labile precursor complex is treated with the olefin, upon which this latter species enters into vacancies of the coordination sphere generated by thermally or photochemically induced dissociation of some ligand.

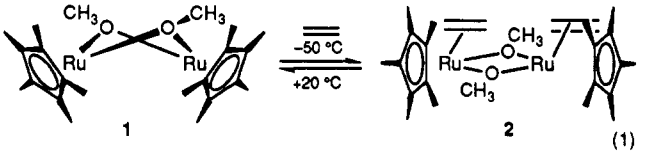
The coordinatively unsaturated Ru complex $[Cp^*Ru(OMe)]_2$ (1),[2-4] in contrast, has been shown to directly add common σ-donor–π-acceptor ligands such as PR_3, bpy, and CO[2,3] with and without cleavage of the dimer, depending on the conditions. The dimer itself offers two vacant coordination sites, and a further ligand may be added to each Ru on cleavage. This bonding situation offers many of the features commonly considered as prerequisites for a catalytically active metal center.

In the following contribution, we described addition and coupling reactions of ethylene, propylene, cyclohexadiene, and cyclooctatetraene with 1.

Results

Reaction of 1 with Ethylene and Propylene. Coordination of olefins to 1, despite the coordinatively unsaturated character of the methoxo complex, does not result in addition of simple mono- or diolefins to give isolable olefin alkoxo complexes under ambient conditions. Chelating 1,5-cyclooctadiene reacts with 1 at ambient temperature in the presence of LiCl by exchange of OMe for Cl and formation of $Cp^*Ru(COD)Cl$[5] or, under hexane reflux over 12 h, with elimination of formaldehyde and formation of the hydride $Cp^*Ru(COD)H$.[6] To further elucidate possible activation of olefins by 1, we have investigated its reaction with ethylene, propylene, and cycloolefins.

When the cherry red solution of 1 in MeOH is saturated at −50 °C with ethylene, the adduct 2 separates as a light yellow precipitate. The color change, characteristic of



1 2 (1)

adduct formation, has been observed with other π-acceptor ligands, e.g. phosphines.[2] However, adduct 2 is readily dissociated into its constituents at room temperature in solution or as a solid. Attempted isolation of the low-temperature compound gave, after warming to room tem-

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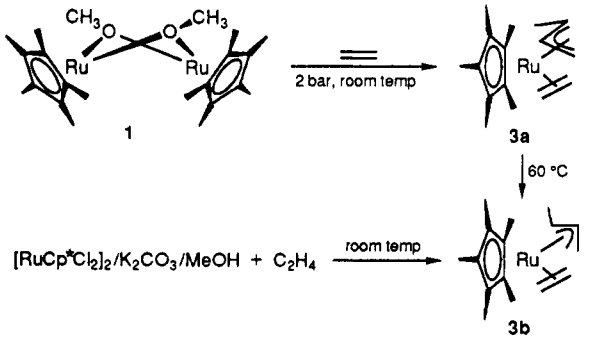
Table I. ^1H and ^{13}C NMR Data (δ (ppm), J (Hz))

		^1H	^{13}C	
		Compound **3a**[a]		
ethylene	H_a	0.71 (d/d, $J_{a,c}$ = 9.3, $J_{a,d}$ = 8)	C_1	43.709
	H_b	2.49 (d/d, $J_{b,d}$ = 9.3, $J_{b,c}$ = 8)		
	H_c	2.204 (d/d)	C_2	41.706
	H_d	2.096 (d/d)		
methallyl	Me	1.71 (d)	C_3	18.383
	H_{a1}	0.017 (d/q, $J_{a1,Me}$ = 6.5)	C_4	64.006
	H_t	3.145 (t/d, $J_{t,a2}$ = $J_{t,a1}$ = 9.5)	C_5	83.349
	H_{a2}	1.235 (d, $J_{s,a2}$ = 1.6)	C_6	39.905
	H_s	2.307 (d/d, $J_{s,t}$ = 6.8)		
	Cp*	1.535 (s)		9.177
			C_{ipso}	91.759
		Compound **3b**[a]		
ethylene	H_a	0.76 (d/d/d, $J_{a,c}$ = 10.5, $J_{a,d}$ = 8.1, $J_{a,b}$ = 1.7)	C_1	37.94
	H_b	0.52 (d/d/d, $J_{b,d}$ = 10.6, $J_{b,c}$ = 8.2)		
	H_c	0.71 (d/d, $J_{c,d}$ = 1.7)	C_2	35.98
	H_d	0.92 (d/d/t)		
methallyl	Me	1.38 (d, $J_{Me,a2}$ = 5.6)	C_6	16.8
	H_{a1}	1.22 (m)	C_5	41.14
	H_t	1.25 (t/d, $J_{t,a1}$ = $J_{t,a2}$ = 8.9)	C_4	93.51
	H_{a2}	0.44 (d/d, $J_{a1,s}$ = 1.2)	C_3	59.05
	H_s	2.43 (d, $J_{s,t}$ = 6)		
	Cp*	1.15 (s)		9.38
			C_{ipso}	93.19
		Compound **4**[b]		
propene	H_a	1.45 (m)	C_1	41.67
	H_b	1.28 (d/t, $J_{b,a}$ = 8.4, $J_{b,c}$ = 1.3)		
	H_c	0.55 (d/d, $J_{c,a}$ = 10.5)	C_2	45.95
	Me	1.19 (d, $J_{a,Me}$ = 6.4)		15.92
allyl	H_{s1}	2.93 (d/d/d, $J_{s1,s2}$ = 1.85, $J_{s1,a1}$ = 0.5)	C_3	42.23
	H_{s2}	2.52 (d/d/d, $J_{s2,a2}$ = 0.3)		
	H_{a2}	0.87 (d, $J_{a2,a1}$ = 1.6)		
	H_{a1}	0.96 (d/d, $J_{a1,a2}$ = 0.6)	C_5	42.2
	H_t	2.17 (t/t, $J_{t,a2}$ = 9.9, $J_{t,s1}$ = 6.4)	C_4	88.7
	Cp*	1.44 (s)		9.59
			C_{ipso}	93.40

[a] Conditions: 500 MHz, solvent C_6D_6. [b] Conditions: 300 MHz, solvent toluene-d_8.

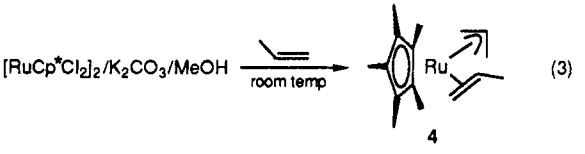
perature, the starting material as the sole product.

When **1** was treated in methanol or hexane at room temperature or at or above room temperature with ethylene under 2 bar of pressure, a slow reaction occurs, evident from a color change to light brown. After 12 h of reaction, the yellow, air-stable complex **3a** could be crystallized from pentane. The pentane-insoluble, waxy residue consisted, according to IR spectroscopy, of polyethylene. If the mixture was heated to 60 °C or, alternatively, if the reaction was conducted as a one-pot synthesis starting from $[Cp^*RuCl_2]_2/K_2CO_3$[7] in MeOH in the presence of ethylene, a second isomer, **3b**, was obtained.



(2)

Further insight into the reaction course was expected from the reaction analogous to (2) with propylene as the olefin. Instead of dimethylallyl complex an unsubstituted allyl ligand was formed, evidently by direct dehydrogenation of propylene attached to Ru. Complex **4** was also readily crystallized and, unlike either isomer of **3**,[8] allowed complete structural characterization by a single-crystal X-ray structure determination.

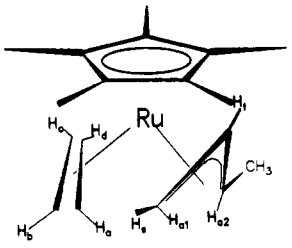


(3)

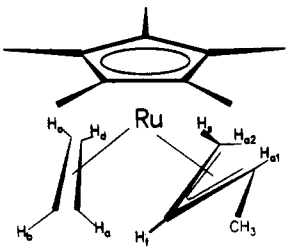
The structure of compounds **3** follows from mass and NMR spectra. The mass spectrum of both isomers **3a** and **3b** shows a molecular mass peak at m/e 320 with loss of 28 mass units in accordance with the formula $Cp^*Ru(C_4H_7)(C_2H_4)$. A 500-MHz ^1H and ^{13}C NMR analysis revealed, besides the presence of a Cp* group, an ABCD pattern for complexed ethylene and a multiplet structure

(7) $[Cp^*RuCl_2]_2/K_2CO_3$/MeOH is the reaction medium to generate **1**.[2,3]

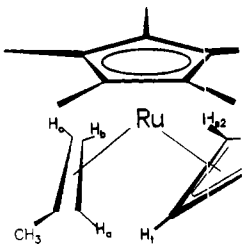
(8) Attempts to determine the structure of either isomer **3** were only partially successful. Though **3a** as well as **3b** readily crystallized from pentane, the molecular model showing Cp*Ru–, C=C, and a C_4 fragment, in the arrangement **3a**, on refinement did not lead to an unambiguous set of bond lengths and bond angles. Obviously not only Cp*Ru but also the allyl ligand is disordered with respect to a crystallographic mirror plane. An attempted low-temperature X-ray analysis of **3b**, on the other hand, was thwarted by a phase transition. Since C_5Me_4Et (Cp*) derivatives often give less disorder problems in crystallography $Cp^*Ru(\eta^3\text{-}C_4H_7)(\eta^2\text{-}C_2H_4)$ was prepared in the same way as **3b** from $[Cp^*RuCl_2]_2$. It was characterized by NMR and mass spectrometry but had a melting point below room temperature.



3a



3b



4

for an η^3-methallyl group. Complete assignment of all proton and carbon signals as listed in Table I was obtained with the aid of ^{1}H–^{1}H COSY and ^{1}H–^{13}C NOESY spectra. The central allylic proton H_t is easily identified by its multiplicity, resonating at relatively low field. The coupling $^3J_{t,a1}$ of 9.5 Hz from the high-field doublet of quartets of H_{a1} equals the larger of the two values of $^3J_{t,a2}$ and $^3J_{t,s}$ (9.5 and 6.8 Hz), placing H_{a1} in the anti and the methyl group in the syn position. Assignment of the four nonequivalent ethylene protons to the two ethylene carbons follows from ^{13}C NOESY spectra.

The shift and coupling parameters yield structure **3a** with a syn-methallyl group bound in the exo mode to Cp*Ru with one molecule of ethylene completing the coordination shell. The orientation of the allyl group (exo or endo) could also be concluded from the X-ray structure analysis of **3a**, though refinement (to an R value of 5%) in this case did not lead to a meaningful set of bond lengths and bond angles for the methallyl group.[8] In the NMR spectra of **3b**, the same pattern of multiplets with different chemical shifts is observed. The principal change with respect to the spectrum of **3a** consists of a high-field shift of H_t from 3.5 ppm in **3a** to ~1.2 ppm in **3b** and a low-field displacement of one of the allylic protons to 2.4 ppm. The coupling $^3J_{t,a1}$ is the same as in **3a**, suggesting the syn/anti orientation of the methyl group to be unchanged. The high-field shift of H_t suggests a methallyl group in the endo orientation as indicated in the formula.

These assignments are in agreement with allyl NMR spectra recently obtained for analogous Cp*Ir complexes.[9] In particular, the high-field shift of H_t and the shift to lower field of the syn and anti protons in the endo as opposed to the exo isomer has been of diagnostic value. Assignments of the NMR shifts of **4** have similarly been obtained with the aid of COSY and NOESY spectra and are indicative of the proposed structure, which for this compound could be verified by an X-ray analysis (see below). Note the shift difference of 0.4 ppm between protons H_{s1} and H_{s2} caused by the asymmetry of the propylene ligand.

It should be further noted that all of the allylic protons of compounds **3** and **4** are at considerably higher field than those commonly observed in Ru–allyl complexes.[10] The rigidity of the olefinic ligands, where no line broadening in the ^{1}H NMR spectrum was observed up to 100 °C,

Table II. Selected Bond Lengths (Å), Bond Angles (deg), and Positional Parameters and Their Estimated Standard Deviations in 4

Bond Distances

Ru–C1	2.257 (4)	Ru–C11	2.171 (5)
Ru–C2	2.206 (4)	Ru–C12	2.137 (5)
Ru–C3	2.195 (4)	Ru–C13	2.190 (5)
Ru–C4	2.237 (4)	Ru–C15	2.160 (4)
Ru–C5	2.278 (4)	Ru–C16	2.143 (5)
C1–C2	1.434 (6)	C11–C12	1.406 (8)
C1–C5	1.402 (6)	C12–C13	1.383 (7)
C2–C3	1.424 (6)	C15–C16	1.431 (7)
C3–C4	1.427 (6)		
C4–C5	1.408 (6)		

Bond Angles

C11–C12–C13	120.2 (6)	C14–C15–C16	123.4 (5)

Positional Parameters[a]

atom	x	y	z	B, Å^2
Ru	0.23235 (3)	0.02355 (2)	0.09510 (2)	3.055 (7)
C1	0.3060 (3)	0.1392 (3)	0.0220 (3)	3.30 (9)
C2	0.3440 (3)	0.1311 (3)	0.1097 (3)	3.8 (1)
C3	0.2660 (3)	0.1492 (3)	0.1689 (3)	3.8 (1)
C4	0.1808 (3)	0.1671 (3)	0.1181 (3)	3.6 (1)
C5	0.2071 (3)	0.1616 (3)	0.0285 (3)	3.28 (9)
C6	0.3654 (4)	0.1359 (4)	−0.0618 (3)	6.0 (1)
C7	0.4494 (4)	0.1161 (4)	0.1330 (4)	6.6 (1)
C8	0.2759 (4)	0.1596 (4)	0.2670 (3)	7.2 (2)
C9	0.0839 (4)	0.1966 (4)	0.1531 (4)	7.4 (2)
C10	0.1425 (4)	0.1824 (3)	−0.0490 (3)	6.0 (1)
C11	0.3129 (4)	−0.0754 (3)	0.0169 (4)	7.0 (2)
C12	0.2149 (5)	−0.1019 (3)	0.0239 (4)	6.6 (2)
C13	0.1420 (5)	−0.0438 (3)	−0.0046 (3)	6.2 (1)
C14	0.0683 (4)	−0.1002 (4)	0.1928 (4)	7.5 (2)
C15	0.1514 (4)	−0.0339 (4)	0.2039 (3)	5.4 (1)
C16	0.2510 (4)	−0.0617 (4)	0.2089 (3)	6.0 (1)
H6A	0.322	0.143	−0.113	7.8
H6B	0.413	0.186	−0.061	7.8
H6C	0.399	0.077	−0.066	7.8
H7A	0.487	0.105	0.079	8.9
H7B	0.475	0.170	0.163	8.9
H7C	0.455	0.062	0.172	8.9
H8A	0.342	0.142	0.285	9.8
H8B	0.264	0.224	0.283	9.8
H8C	0.229	0.120	0.297	9.8
H9A	0.085	0.194	0.218	8.9
H9B	0.071	0.260	0.134	8.9
H9C	0.033	0.156	0.130	8.9
H10A	0.077	0.196	−0.028	7.4
H10B	0.168	0.236	−0.081	7.4
H10C	0.141	0.129	−0.089	7.4
H11A	0.363	−0.101	0.056	9.2
H11B	0.327	−0.044	−0.038	9.2
H12	0.191	−0.156	0.056	8.7
H13A	0.146	−0.004	−0.057	7.9
H13B	0.077	−0.060	0.016	7.9
H14A	0.052	−0.129	0.249	9.0
H14B	0.088	−0.148	0.151	9.0
H14C	0.011	−0.068	0.170	9.0
H15	0.129	0.014	0.244	7.3
H16A	0.300	−0.027	0.242	8.4
H16B	0.269	−0.123	0.188	8.4

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3)]$; hydrogen atoms have been assigned an isotropic thermal parameter of $B_H = 1.3B_C$.

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(10) (a) Cp*RuX$_2$(η^3-C$_3$H$_5$): Nagashima, H.; Katsunori, M.; Shiota, Y.; Yamagushi, K.; Ara, K.-I.; Fukahori, T.; Suzuki, H.; Akita, M.; Moro-oka, Y.; Itoh, K. *Organometallics* **1990**, *9*, 799. (b) Ru(η^3-C$_3$H$_5$)(CO)$_3$Br: Wuu, Y.-M.; Wrighton, M. *Organometallics* **1988**, *7*, 1839. (c) CpRu(CO)(η^3-C$_3$H$_5$): Gibson, D. H.; Hsu, W.-L.; Steinmetz, A. L.; Johnson, B. V. *J. Organomet. Chem.* **1981**, *208*, 89.

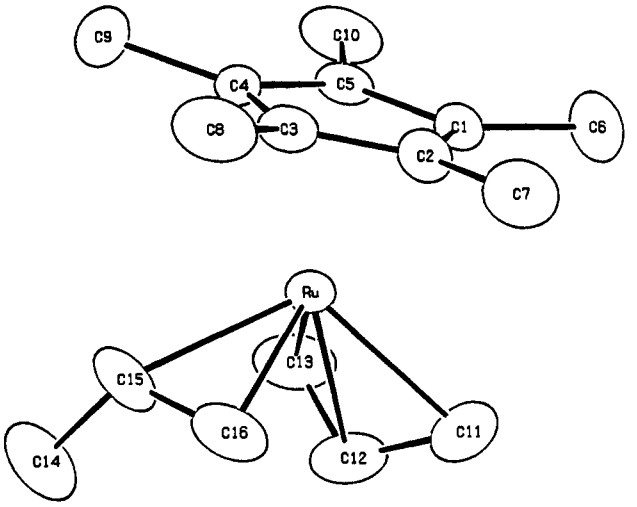


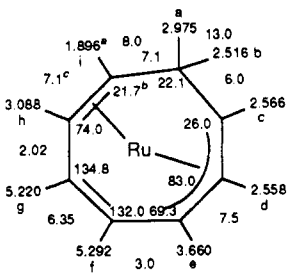
Figure 1. ORTEP drawing of $Cp^*Ru(\eta^3\text{-}C_3H_5)(\eta^2\text{-}C_2H_3CH_3)$ (**4**).

points in the same direction. The conformational stability of these Ru(II) allyl complexes in the olefin as well as in the allyl part parallel their thermodynamic stability. Often allyl complexes are amenable to further insertion of olefins to form higher oligomers.[11] No signs of further reaction of **3** with ethylene under 3 bar at 100 °C were found.

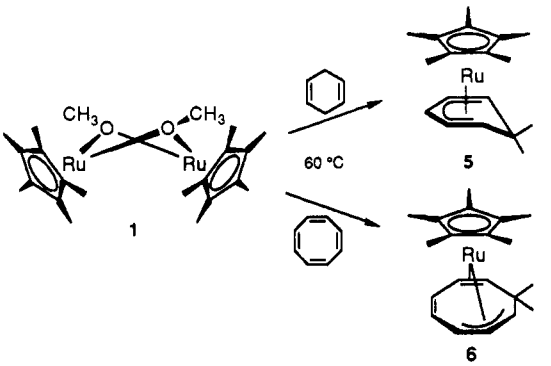
Structure of 4. Crystals of **4** were obtained from pentane at low temperature. The compound crystallizes in the space group *Pbca* with a = 13.752 (3) Å, b = 14.576 (2) Å, c = 15.174 (4) Å, and Z = 8. An ORTEP drawing of the molecule is shown in Figure 1, a selection of bond lengths is given in Table II. Figure 1 shows a Cp*Ru fragment with η^2-coordinated propylene and η^3-coordinated allyl in the endo orientation. The distance of Ru to the central carbon C(12) (2.137 (5) Å) is less than that to the terminal carbons C(11) (2.171 (5) Å) and C(13) (2.190 (5) Å) as found in many endo-allyl complexes. The asymmetry in the ^{1}H NMR signals of the syn and anti allylic protons is hardly reflected in Ru–C bond lengths; in the allylic as well as in the olefinic part they are equal within 6 pm. Allylic carbon–carbon distances are at the short end for π-allyl complexes and compare well with the analogous parameters in exo and endo isomers of $CpRu(2\text{-}MeC_3H_4)(CO)$,[12] whereas Ru–allyl carbon distances are shorter than in these closely related complexes, which indicates a relatively high population of the allylic ψ_1 orbital and little back-bonding from Ru into allyl MO's. Thus, Ru acts mainly as an acceptor toward the allyl ligand, in line with the high-field shifts observed in the NMR spectra. Bond lengths in the olefinic part are indicative of a fair amount of Ru to olefin back-bonding.

Reaction of 1 with Cyclic Dienes. A reaction largely similar to that occurring with ethylene and propylene was found with 1,4-cyclohexadiene. At methanol reflux temperature, the cyclic diene is dehydrogenated to a cyclohexadienyl ligand complexed to Ru (complex **5**). The isolated yield in this reaction is only about 50%; one of the side products found is the dinuclear complex $[Cp^*Ru(\mu\text{-}H)CO]_2$ previously observed[13] as one of the thermolysis products of **1**. The structure of **5** is established easily from spectroscopic and analytical data (see Experimental Section); the analogous Cp compound has been described.[14]

Chart I. Chemical Shifts and Coupling Constants[a] in Complex 6



[a] ^{1}H chemical shift (δ). [b] ^{13}C chemical shift (δ). [c] ^3J coupling (Hz).



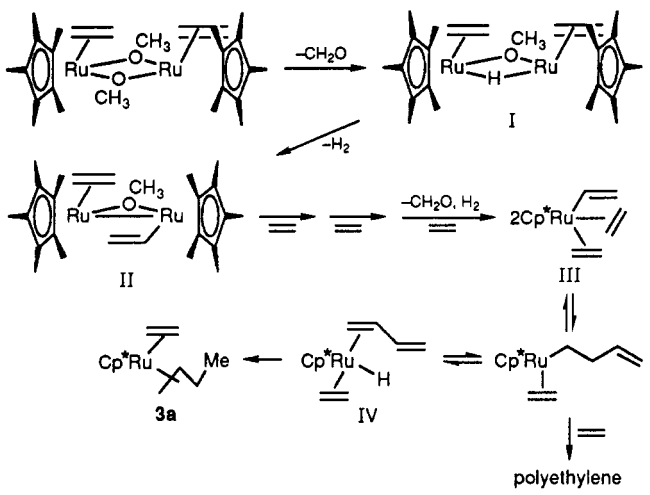
Similarly, cyclooctatetraene reacted under the same conditions to give the cyclooctatrienyl complex **6**, where the ligand has been hydrogenated. The composition of **6** again follows from spectroscopic data (Chart I). In (500 MHz) ^{1}H and ^{13}C NMR spectra, individual proton multiplets and carbon signals were observed for all nine nonequivalent protons and the eight carbon atoms of the π-cyclic ring. The compound does not show any fluxionality at ambient temperature on the NMR time scale.[15] Assignments were derived from COSY, NOESY, and INEPT spectra, leaving the relative positions of protons H_d and H_c, which closely coincide with one of the methylene protons H_a or H_b in an incompletely resolved three-proton multiplet, as the sole ambiguity. A split AB pattern at low field is assigned to uncomplexed olefinic protons H_g and H_f. Neighboring protons H_e and H_h are identified through their small couplings to these low-field multiplets and adjacent protons by the larger coupling constants. $C_{a,b}$ is found from the INEPT spectrum as the methylenic carbon, and protons H_a and H_b are located at this carbon from the ^{1}H–^{13}C NOESY spectrum. The bonding mode of the Cp*Ru unit to the cyclooctatrienyl moiety with one isolated, noncomplexed double bond is the only one compatible with the spectroscopic data.

Discussion

Coupling of olefins to form complexed allyl ligands at Ru is not without precedence.[16] Apart from the widely

(11) Strana, G.; Brala, G.; Benedetti, E. *J. Chem. Soc., Dalton Trans.* **1975**, 754.
(12) Hsu, L.-Y.; Nordman, C. E.; Gibson, D. H.; Hsu, W.-L. *Organometallics* **1989**, *8*, 241.
(13) Koelle, U.; Kang, B.-S.; Thewalt, U. *Organometallics* **1991**, *10*, 2569.
(14) Robertson, D. R.; Stephenson, T. A. *J. Organomet. Chem.* **1977**, *142*, C31.
(15) See: Deganello, G. *Transition Metal Complexes of Cyclic Polyolefins*; Academic Press: London, 1979; p 277ff. (η^5-Cyclooctatrienyl)(η^4-cyclooctadiene)rhodium and (η^5-cyclooctatrienyl)(η^4-norbornadiene)rhodium: *Ibid.*, p 256. (η^5-Cyclooctatrienyl)(η^5-cyclopentadienyl)iron: *Ibid.*, p 195. (η^5-Cyclooctatrienyl)tricarbonylmanganese.

Scheme I



recognized oxidative coupling of two coordinated olefins to a metallacyclopentane followed by β-elimination,[17] a mechanism where the key step consists in insertion of ethylene into a metal–vinyl bond must be considered as a plausible alternative in the formation of the C_4 fragment at Ru. Lehmkuhl et al.[16] had obtained a $Cp(PR_3)_2Ru$–vinyl complex through activation of the vinylic =CH bond of styrene. Suzuki et al.[18] had observed the formation of vinyl complexes in the reaction of the dimeric hydride $(Cp^*Ru)_2(\mu\text{-}H)_4$ with ethylene under very mild conditions. Considering the fact that the closely related carbonyl hydride complex $(Cp^*Ru)_2(\mu\text{-}H)_2(\mu\text{-}CO)$ is formed from 1 under a wide variety of conditions,[13] the intermediate formation of vinyl complexes gains much probability.

Starting from $CpRu(PPh_3)_2(\sigma\text{-}CH{=}CH_2)$, Lehmkuhl et al.[16] obtained the methallyl complex $CpRu(PPh_3)(\eta^3\text{-}CH_2CHCHMe)$ under 30 bar of ethylene at 150 °C in 85% yield. The syn,exo isomer in this case was the thermodynamically stable form. Ethylene insertion into a Ru–vinyl bond could proceed much easier at the coordinatively unsaturated fragments depicted in Scheme I than in the phosphine-stabilized vinyl complexes of Lehmkuhl. Therefore, reaction conditions in the present case can be much milder.

Scheme I depicts a possible sequence starting from the low-temperature addition product **2**, which may be present in equilibrium at room temperature to a small extent. Aldehyde elimination, facilitated through the coordination of an olefin,[19] leads to the hydride I, which can generate the first vinyl intermediate II analogous to Suzuki's tetrahydride. Repetition of the reaction sequence at either the mono- or dinuclear complex could lead to intermediate III, from where the reaction follows the steps generally discussed in olefin oligomerization at transition-metal centers.

In the reaction of 1 with cyclic olefins either hydrogenation or dehydrogenation occurs as required to form an 18-electron product. Both pathways can be rationalized on the basis of Scheme I. Hydrogenation can occur from an intermediate analogous to I by transfer of the bridging hydrogen and dehydrogenation by β-elimination from the olefin complex analogous to I to form a dihydride with ensuing loss of dihydrogen.

No signs of addition products of methanol to the olefin have been detected in the reaction mixture. It should be noted that the temperature at which reactions 1–3 proceed is well below the decomposition temperature of complex 1.[13] Whereas the thermolysis of 1 in the absence of a coordinating molecule requires 95 °C and leads to binuclear complexes $[(Cp^*Ru(\mu\text{-}H))_2(\mu\text{-}CO)]$, $[Cp^*Ru(\mu\text{-}H)(CO)]_2$, and $[Cp^*Ru(\mu\text{-}CO)(CO)]_2$,[13] this temperature is lowered to 60 °C in the presence of cyclic polyenes or to ambient temperature in the case of ethylene and propylene.

The much milder conditions required for the formation of **3** and **4** in contrast to those for similar transformations at CpRu–phosphine complexes[16] are paralleled by the room-temperature olefin activation at the solvento cation $Cp^*Ir(S)_3^{2+}$ [9] and nicely illustrate the ability of coordinatively unsaturated complexes in olefin (and other functional group) activation. Finally, the ease with which complexes **3** and **4** are formed is considered responsible for the low proportion of polyethylene formed in reaction 2.

The cyclooctatrienyl complex **6** is not fluxional at ambient temperature and again resembles in this respect its cationic CpIr congener $[CpIr(C_8H_9)]^+$, where the same bonding mode as was derived from spectroscopic data for **6** was assumed.[15] This nonfluxionality can be interpreted in terms of the capability of a Cp^*Ru^{II} fragment for strong back-bonding into the cyclooctadienyl ligand as compared to M(olefin) or M(carbonyl) moieties. The high yield in which the complex is formed and the inertness of the yellow crystals to atmospheric oxygen point in the same direction. Incorporation of the olefinic double bond into the bridging alkoxide again changes the decomposition and transformation chemistry of type 1 complexes and will be the subject of a further communication.[19]

Experimental Section

All experiments were conducted under nitrogen with absolute, nitrogen-saturated solvents using conventional Schlenk techniques. IR spectra were recorded on a Perkin-Elmer 842 spectrometer and ^1H and ^{13}C NMR spectra on Bruker SY 80 and Varian VXR 300 and Unity 500 instruments. Mass spectra were obtained at 70 eV nominal electron energy with a Varian CH-5 DF spectrometer. Elemental analyses were by Analytische Laboratorien, Engelskirchen, Germany.

(η^2-Ethylene)(η^3-*exo*-*trans*-but-1-en-3-yl)(pentamethylcyclopentadienyl)ruthenium (3a). In a thick-walled Schlenk tube equipped with a pressure-tight PE valve was placed 0.21 g of 1 (0.78 mmol of Ru) in 20 mL of MeOH and the flask pressurized with 2 bar of ethylene. After 12 h at ambient temperature the solvent was evaporated in vacuo, the residue extracted with pentane, and this extract filtered and concentrated to 3 mL. The pentane solution was chromatographed on a 4 × 1.5 cm Al_2O_3 column (5% H_2O), and a yellow band eluted with pentane was collected. Pentane was stripped off and the residue dissolved in $MeOH/Et_2O$ and crystallized at −80 °C. The yield was 0.13 g (52%) of yellow needles. ^1H NMR: see Table I. MS (m/z (I_{rel})): 320 (52, M^+), 292 (90, M − C_2H_4), 290 (100, M − C_2H_6), 236 (70, Cp*Ru − H). Anal. Calcd for $C_{16}H_{26}Ru$ (M_r 319.4): C, 60.16; H, 8.20. Found: C, 60.51; H, 8.15.

(η^2-Ethylene)(η^3-*endo*-*trans*-but-1-en-3-yl)(pentamethylcyclopentadienyl)ruthenium (3b). In a thick-walled Schlenk tube as above were placed 1.92 g of K_2CO_3 and 0.64 g of $[Cp^*RuCl_2]_2$ (2.08 mmol of Ru) in 40 mL of MeOH. The flask was pressurized with 2 bar of ethylene. After the mixture was stirred for 6 h at ambient temperature, the solvent was evaporated and further workup procedure was as described for **3a**. The yield was 0.59 g (90%) of yellow needles. ^1H NMR: see Table I. MS:

(16) (a) Lehmkuhl, H.; Grundke, J.; Mynott, R. *Chem. Ber.* **1983**, *116*, 176. (b) Lehmkuhl, H.; Bellenbaum, M.; Grundke, J.; Mauermann, H.; Krüger, C. *Chem. Ber.* **1988**, *121*, 1719.

(17) Keim, W.; Behr, A.; Röper, M. In *Comprehensive Organometallic Chemistry*; Pergamon Press: London, 1982; Vol. 8, p 371ff.

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(19) Koelle, U.; Kang, B.-S.; Thewalt, U. *Organometallics*, submitted for publication.

Table III. Summary of Crystallographic Data for $Cp^*Ru(\eta^3\text{-}C_3H_5)(\eta^2\text{-}CH_2CHCH_3)$

molecular formula	$C_{16}H_{26}Ru$
fw	319.46
cryst syst	orthorhombic
space group	*Pbca*
cell dimens (20 °C)	
a, Å	13.752 (3)
b, Å	14.576 (2)
c, Å	15.174 (4)
V, Å^3	3042 (2)
Z	8
d_{calcd}, g/cm^3	1.395
cryst dimens, mm	0.3 × 0.3 × 0.5
radiatn, Å	λ(Mo Kα) = 0.7093
data collection method	ω
θ scan range, deg	3.0 ≤ θ ≤ 23.0
total no. of data	2689
no. of unique obsd data, $I > 3\sigma(I)$	1534
abs coeff (μ), cm^{-1}	9.91
method of refinement	full-matrix least squares
no. of variables	154
R	0.027
R_w	0.035
weighting factor, *w*	$1/\sigma^2[F_o]$
goodness of fit	1.24
Δρ(max), e Å^{-3}	0.36, 1.2 Å from Ru

as for **3a**. Anal. Calcd for $C_{16}H_{26}Ru$ (M_r 319.4): C, 60.16; H, 8.20. Found: C, 60.11; H, 8.24.

(η^2-Propylene)(η^3-*endo*-prop-1-en-3-yl)(pentamethylcyclopentadienyl)ruthenium (4). Using 1.02 g of K_2CO_3 and 0.34 g of $[Cp^*RuCl_2]_2$ (1.10 mmol of Ru) in 30 mL of MeOH and propene instead of ethylene, the same procedure as for **3b** was followed. The yield was 86% of cube-shaped off-white crystals. $^1H/^{13}C$ NMR: see Table I. MS (m/z (I_{rel})): 320 (35, M^+), 278 (100, M − C_3H_6), 236 (100, Cp^*Ru − H). Anal. Calcd for $C_{16}H_{26}Ru$ (M_r 319.4): C, 60.16; H, 8.20. Found: C, 59.97; H, 8.07.

((1-5-η)-Cyclohexadienyl)(pentamethylcyclopentadienyl)ruthenium (5). A solution of 0.23 g of **1** (0.86 mmol of Ru) and 100 μL of 1,4-cyclohexadiene (1.04 mmol) in 20 mL of hexane was refluxed for 12 h. The color changed from cherry red to brown. After the solution was evaporated to dryness, the residue was extracted with pentane and chromatographed over Al_2O_3 (5% H_2O). A yellow band was eluted with pentane/toluene (10:1). After evaporation to dryness, redissolving in pentane and filtration the solution was concentrated and the product crystallized at −80 °C as yellow needles. The yield was 0.12 g (45%). ^1H NMR (C_6D_6): δ 5.32 (t, 1 H), 4.12 (dd, 2 H), 2.15 (m, 2 H), 2.59 (t, 1 H), 1.48 (m, 1 H), 1.94 (s, 15 H). MS (m/z (I_{rel})): 315 (90, M − H), 301 (100, M − CH_3), 233 (85, Cp^*Ru − 4 H). Anal. Calcd for $C_{16}H_{22}Ru$ (M_r 315.1): C, 60.93; H, 7.03. Found: C, 60.54; H, 6.71.

((1,2,5-7-η)-Cycloocta-1,3,5-trien-7-yl)(pentamethylcyclopentadienyl)ruthenium (6). A solution of 0.15 g of **1** (0.56 mmol of Ru) and 60 μL (0.56 mmol) of cyclooctatetraene in 20 mL of MeOH was stirred for 6 h at 60 °C, whence the color changed from red to brown. The residue remaining after evaporation of the solvent was dissolved in pentane and the solution absorbed on a 1-cm column of Al_2O_3 (5% H_2O) and eluted with about 100 mL of pentane. After the solution was concentrated to 2 mL, the product crystallized at −80 °C as yellow needles. The yield was 0.17 g (90%). ^1H NMR (C_6D_6): Chart I, 1.57 (s, Cp^*). MS (m/z (I_{rel})): 341 (70, M − H^+), 327 (100, M − CH_3), 315 (98, M − C_2H_3), 233 (60, Cp^*Ru − 4 H). Anal. Calcd for $C_{18}H_{24}Ru$ (M_r 341.1): C, 63.31; H, 7.08. Found: C, 63.64; H, 7.18.

Crystal Structure Determination. Single crystals of **4** were grown from pentane solution at low temperature. Crystal data together with details of the X-ray diffraction experiment are collected in Table III. The compound crystallizes in the orthorhombic space group *Pbca* (No. 61) with a = 13.752 (3) Å, b = 14.576 (2) Å, and c = 15.174 (4) Å. Data were collected at 20 °C with an Enraf-Nonius CAD-4 diffractometer. Corrections for Lorentz–polarization and absorption (empirically using ψ scans[20]) were carried out using the SDP program system.[21] Of the 2689 reflections measured in the range of $3 < \theta < 23°$, 1534 were unique with $I > 3\sigma(I)$ and were used for structure solution and refinement. The structure was solved by Patterson and Fourier difference maps. Methyl hydrogen atoms were calculated at idealized positions. Hydrogen atoms at allyl and ethylene carbons were located in one difference Fourier map. Their distances were normalized to 0.98 Å while bond and dihedral angles were retained. All hydrogen atoms were treated as "riding" in the final refinement. Thermal parameters for hydrogen atoms were set as $B_H = 1.3B_C$. The least-squares refinement (x, y, z, and U_{ij} for non-hydrogen atoms) converged with the agreement factors R = 0.027 and R_w = 0.035, using a statistical weighting scheme of $w = 1/\sigma^2[F_o]$.

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Registry No. **1**, 120883-04-7; **3a**, 137436-46-5; **3b**, 137492-97-8; **4**, 137436-47-6; **5**, 137436-48-7; **6**, 137464-61-0; $[Cp^*RuCl]_2$, 123661-80-3.

Supplementary Material Available: Tables of anisotropic temperature factors and bond distances (2 pages); a table of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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(21) Frenz, B. A. In *Computing in Crystallography*; Schenk, H. Olthof-Hazekamp, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, The Netherlands, 1987; SDP-Plus, Version 1.1 (1984), and VAXSDP, Version 2.2 (1985).