Organometallics 1992, *11*, 2893–2899

Reactions of $[Cp^*RuOMe]_2$. 10.[1] Synthesis, Structure, and Transformations of $[Cp^*Ru(\mu\text{-}\eta^3\text{-}O(CH_2)_2CH{=}CH_2)]_2$, an Alkoxide-Bridged Dimer Destabilized by Internal π-Coordination[†]

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The Ru alkoxo complex $[Cp^*RuOMe]_2$ (1) reacts with but-3-en-1-ol below room temperature with exchange of the alkoxo group to yield the respective butenyloxy dimer $[Cp^*Ru(\eta^3\text{-}O(CH_2)_2CH{=}CH_2)]_2$ (2), which was characterized by an X-ray structure determination (orthorhombic space group *Fdd*2, $Z = 8$, 4 pairs of enantiomers, $a = 38.936$ (2) Å, $b = 8.976$ (2) Å, $c = 15.406$ (3) Å). In 2 the olefinic double bonds are coordinated to Ru, leading to a flattened Ru–O–Ru–O rhombus. Complex 2 shows enhanced thermal and substitutional reactivity compared to 1. On reaction with two-electron ligands L (L = PPh_3, $CH_2{=}CH_2$, $PhCH{=}CH_2$, $PhC{\equiv}CPh$) the butenyloxy group is transformed into an allenecarboxaldehyde ligand, giving the complexes $Cp^*Ru(\eta^3\text{-}CH_2CHCH\text{–}CHO)L$. Acrylic acid substitutes a methoxy group in 1, yielding $Cp^*Ru(\eta^2\text{-}O_2CCH{=}CH_2)(\eta^2\text{-}CH_2{=}CHCOOH)$ (12) and, on addition of PPh_3, $Cp^*Ru(\eta^3\text{-}O_2CCH{=}CH_2)PPh_3$ (13).

Alkoxo complexes of the Pt metals form an interesting class of compounds due to their widespread reactivity.[2] Many of them are inherently unstable, converting easily to hydrides via β-elimination, and factors that influence their stability are not fully understood. Other transformations include insertions into the metal–oxygen bond or cleavage of this bond by electrophiles and nucleophiles.

A special case of this class of compounds is provided by bridged alkoxo species, where two oxygen electron pairs are engaged in metal bonding, which tends to lead to an overall stabilization of the metal alkoxide arrangement.[3,4]

In the dimeric Ru alkoxide $[Cp^*RuOMe]_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$; 1)[4,5] Ru has a vacant coordination site and is thought to be stabilized by π-bonding from oxygen lone pairs into Ru d orbitals.[5] The characteristic folded-up or butterfly conformation of the Ru–O–Ru–O rhombus rests on this interaction. Consequently, this conformation is lost on completion of the metal coordination shell when acceptor ligands such as CO[5] and phosphines[6] are added to the dimer.

Complex 1 and its higher alkoxy congeners (up to *n*-Bu has been prepared[4]) show remarkable thermal stability toward aldehyde elimination and formation of hydrides. If under forcing conditions (95 °C is required for 1 to decompose in toluene[7]) or, alternatively, through elimination of one alkoxo group through electrophilic or nucleophilic exchange[7] the alkoxo bridge is partially broken, the remaining fragment, due to its highly unsaturated and destabilized nature, shows C–H and other bond-activating properties, which causes rupture of all carbon–hydrogen and carbon–carbon bonds of the remaining bridging alkoxide group, transforming it into CO and hydrogen coordinated to a dimeric $Cp^*Ru{\equiv}RuCp^*$ unit in $Cp^*Ru(\mu\text{-}H)_2(\mu\text{-}CO)RuCp^*$ (3) (see eq 4).

Previous work[1,8,9] has further shown that olefins, unlike CO, phosphines, and other two- or four-electron ligands, do not readily coordinate to 1 under ambient conditions. Reaction with olefins, occurring at higher olefin pressure or elevated temperatures (65 °C), led to elimination of the alkoxide and coordination of the olefin consecutive to its transformation by hydrogenation/dehydrogenation or coupling.[1] We sought to facilitate this process by incorporating a bridging alkoxide possessing an olefinic double bond that might be able to complex to the vacant metal coordination site. Concomitantly, the geometry of the molecule would be altered in such a fashion that Ru becomes a center of chirality, which would eventually allow stereochemical control of substitution reactions. The change in the complex geometry and in reactivity would give further hints toward an interpretation of the unusual bonding and reaction properties of complexes 1. The results of these studies are presented here.

Results

Reaction of $[Cp^*RuOMe]_2$ with Unsaturated Alcohols. Since it has been observed that the most easy access to 1, i.e. reaction of $[Cp^*RuCl_2]_2$ with methanol in the presence of K_2CO_3 as neutralizing agent, with higher alcohols gives steadily decreasing yields,[4] alkoxide exchange in the alkoxo dimer, which has been studied for R = Me, Et[4,5] was chosen as the synthetic approach to complexes

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[†] Dedicated to Prof. Dr. Hermann Stetter on the occasion of his 75th birthday, May 16, 1992.

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(1) Part 9: Koelle, U.; Kang, B.-S.; Spaniol, Th.; Englert, U. *Organometallics* **1992**, *11*, 249.

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(3) For a review see: Mehrotra, R. C.; Agarwal, S. K.; Singh, Y. P. *Coord. Chem. Rev.* **1985**, *68*, 101.

(4) (a) Koelle, U.; Kossakowski, J. *J. Chem. Soc., Chem. Commun.* **1988**, 549. (b) Koelle, U.; Kossakowski, J. *J. Organomet. Chem.* **1989**, *362*, 383. (c) Koelle, U.; Kossakowski, J.; Boese, R. *J. Organomet. Chem.* **1989**, *378*, 449.

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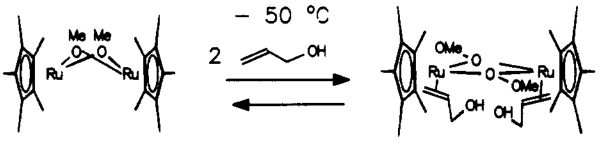
featuring bridging groups other than methoxy. Reaction of 1 with unsaturated alcohols proceeded below room temperature and was performed at −18 °C in ether solution with allyl alcohol, 3-butenol, 4-pentenol, and *cis*- and *trans*-3-hexenol.

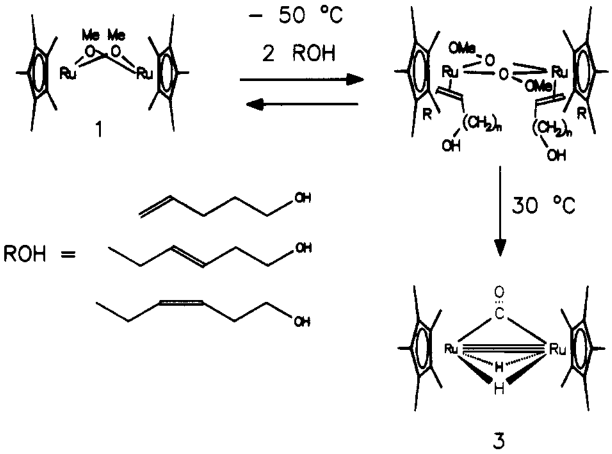
In each case a yellow precipitate was formed at low temperature indicative of addition of the C═C double bond to the vacant coordination site (eq 1) depicted in 4 for allyl alcohol, as has been observed with other olefins.[1] Adduct 4, like the ethylene analogue,[1] dissociates at room temperature.



1 4 (1)

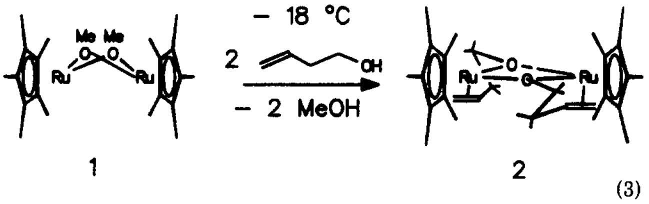
At ambient temperature allyl alcohol applied in excess gave exchange of the alkoxo group to yield a dark violet material that was very soluble in pentane and could not be crystallized from any solvent. The very air-sensitive oil that remained after evaporation of the solvent has not been further characterized but seemed to contain no coordinated olefinic double bonds.

4-Pentenol as well as *cis*- and *trans*-3-hexenol also seemed to react with 1 at low temperature with addition of an olefinic double bond, as can be seen by a color change from red to light brown. Warming to room temperature in each case gave the hydride $Cp^*Ru(\mu\text{-}H)_2(\mu\text{-}CO)RuCp^*$ (3) as the only isolable reaction product in high yield (eq 2). Thus, exchange of the alkoxide occurred but the intermediates reacted further in the sense of the previously observed C–H activation.[7]



(2)

Reaction of 1 with 3-butenol at ambient temperature also produced complex 3, whereas at −20 °C, the lowest temperature at which exchange was reasonably fast, the product of alkoxide exchange $[Cp^*Ru(OC_4H_7)]_2$ (2) (eq 3) was obtained. It was isolated in over 90% yield by crystallization from pentane as red-brown crystals.



1 2 (3)

The fragment of highest mass in the mass spectrum of 2, m/z = 544, conforms to $(Cp^*Ru)_2OC_4H_7$ and can be traced back to a dimer which has lost one butenoxo group.

Chart I. NMR Parameters for Compounds 2 and 7

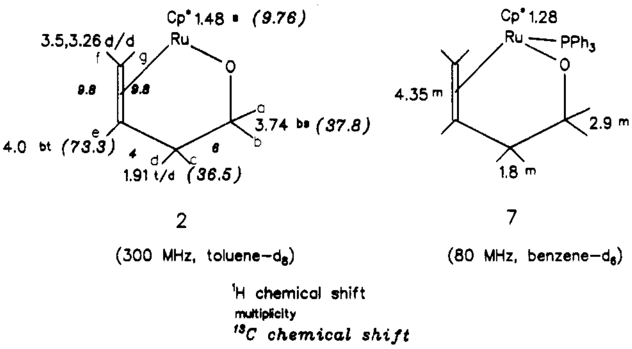


Table I. Bond Distances (Å) and Angles (deg) in 2

Ru–O	2.163 (6)	Ru–C1	2.277 (10)
Ru–O′	2.130 (6)	Ru–C2	2.146 (10)
Ru′–O	2.130 (6)	Ru–C3	2.152 (10)
Ru′–O′	2.163 (6)	Ru–C4	2.192 (10)
Ru–C13	2.138 (10)	Ru–C5	2.295 (11)
Ru–C14	2.165 (12)	C1–C2	1.430 (14)
O–C11	1.426 (12)	C1–C5	1.409 (15)
C11–C12	1.566 (15)	C2–C3	1.438 (14)
C12–C13	1.506 (15)	C3–C4	1.448 (14)
C13–C14	1.422 (15)	C4–C5	1.445 (15)
O–Ru–O′	72.7 (2)	Ru–O–C11	118.9 (5)
O–Ru′–O′	72.2 (2)	Ru′–O–C11	116.5 (5)
O–Ru–C13	124.7 (3)	O–C11–C12	106.5 (8)
O–Ru–C14	92.6 (3)	Ru–C13–C12	108.7 (7)
O′–Ru–C13	78.7 (3)	Ru–C13–C14	71.7 (6)
O′–Ru–C14	86.2 (3)	C11–C12–C13	110.2 (8)
C13–Ru–C14	38.6 (4)	C12–C13–C14	123.7 (9)
Ru–O–Ru′	106.9 (3)	Ru–C14–C13	69.7 (6)
Ru–O′–Ru′	106.9 (3)		

The ^1H NMR spectrum of 2 (Chart I) shows multiplets due to olefinic protons at 4.18, 3.52, and 3.26 ppm, shifted to higher field from their position in the olfinic alcohol by about 1.5 ppm. CH_2O protons H_a and H_b are assigned to the multiplet at 3.74 and H_c and H_d to an AB pattern at 1.9 ppm. The assignment was made with the aid of a COSY spectrum, showing strong coupling of H_a and H_b to H_c and H_d, coupling of the latter group to H_e, and coupling of H_e to H_c and H_d and to the terminal olefinic protons H_f and H_g.

The high-field shift of the olefinic protons along with the more brownish color of the complex in solution, which has been found to be characteristic for addition products of 1, suggests internal complexation of the olefinic double bond. The mass spectrum points to a dimeric structure which, together with coordinated double bonds, would yield two coordinatively saturated 18-electron Ru centers. These conclusions are confirmed by a structure determination for 2.

Molecular Structure of 2. Complex 2 crystallizes in the space group *Fdd*2 with $Z = 8$ as four pairs of enantiomers. A selection of bond lengths and bond angles is given in Table I. The principal arrangement (hydrogen atoms omitted), shown in Figure 1, consists of a near-planar (sum of Ru–O–Ru and O–Ru–O angles 359.2°) Ru–O–Ru–O rhombus, topped on one face by Cp* rings and η^3-bound to butenoxy groups through oxygen and the terminal C═C double bond on the opposite face, imposing C_2 symmetry on the molecule. The flattening of the central Ru–O–Ru–O core, which is folded in the starting complex 1, has previously been found by Tilley et al.[5] in the CO adduct $[Cp^*RuOC_2H_5(CO)]_2$ (5), where the CO groups likewise add cis to the $[Cp^*Ru(OC_2H_5)]_2$ frame, and has

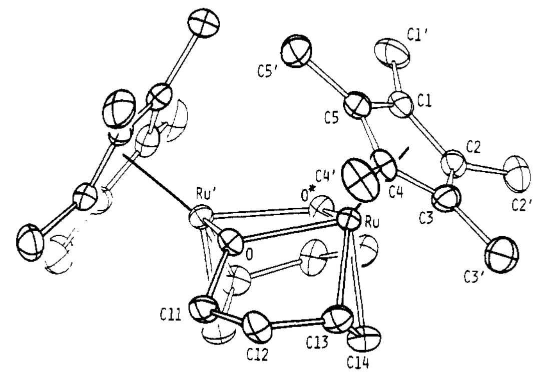


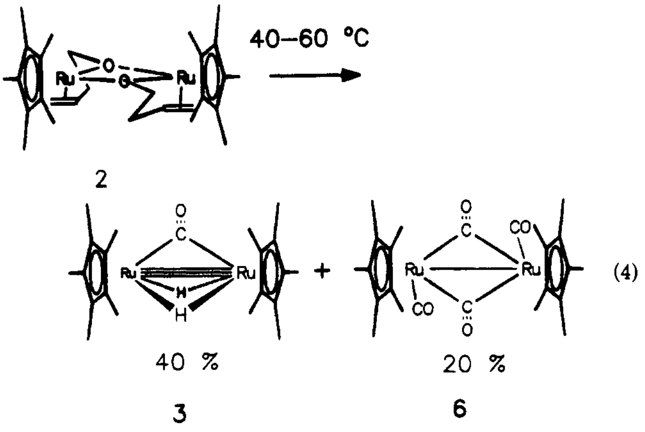
Figure 1. ORTEP drawing of 2 with 20% probability ellipsoids.

again been observed in the diphos addition product [Cp*Ru(OH)]$_2$dppm.[6] The dihedral angle subtended by O–Ru–O planes is 124° in 1 and 162.5° in 5 but 171° in 2. This could be due not only to a larger steric constraint in 2 but also to a stronger donor function of the olefin.

In a comparison of bond distances in 2 to those in Ru(η^5-C$_8$H$_{11}$)(η^3(*O,C,C'*)-OCOCH$_2$CH=CH$_2$)PMe$_3$,[10] where the crotonic acid is coordinated through one oxygen and a double bond, it is obvious that Ru–C bond distances in 2 are shorter (2.138 (10), 2.165 (10) vs 2.22, 2.20 Å) and olefinic C=C distances are longer (1.422 (15) vs 1.372 Å) than in this complex and closer to the ones found in an olefin coordinated to a Cp*Ru(η^3-allyl) moiety,[1] indicating a high degree of Ru–olefin back-bonding. Furthermore, Ru–O distances have lengthened from 2.05 Å in 1 to 2.13/2.16 Å in 2. Thus, as was the case in 5, lengthening of the Ru–O bond length goes along with flattening of the Ru–O–Ru–O core due to loss of Ru–O π-bonding. The Ru–O–Ru angles have widened from 92° in 1 to 107° in 2 along with an increase in Ru–Ru distance from 2.95 to 3.54 Å.

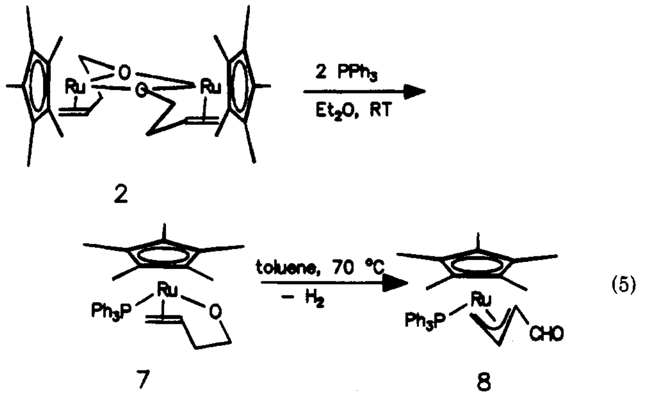
Thermolysis and Reaction with Two-Electron Ligands. The change from a 16- to an 18-VE (VE = valence electron) complex with concomitant changes in geometry also alters the reactivity of 2 as compared to 1, but in a sense opposite to what might have been expected. Whereas addition of two-electron-donor ligands is easier with 1, the thermal stability of 1 is considerably higher than that of 2 and the coordinatively saturated complex 2 reacts with olefins more readily and reacts in a different manner than the unsaturated complex 1.

Thermolysis of 2 (eq 4) starts at about 40 °C. If conducted at 60 °C, 3 is isolated as the main decomposition product after chromatography in 40% yield along with 20% of the dimeric dicarbonyl [Cp*Ru(CO)(μ-CO)]$_2$ (6), the remainder being insoluble decomposed material. Monitoring the reaction by NMR spectroscopy in toluene-d_8 only revealed a gradual decrease in the intensities of the olefinic protons of 2, the final spectrum is that of the mixture of 3 and 6.



(4)

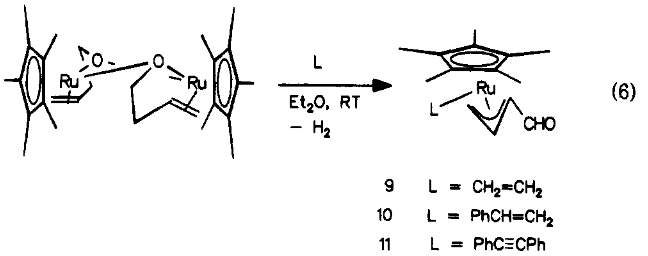
Addition of a two-electron ligand to 2 is expected to cleave the dimer to a stable monomeric, easy to characterize 18-electron species. This type of reaction (eq 5) was observed with PPh$_3$, which formed the phosphine adduct Cp*Ru(OC$_4$H$_7$)(PPh$_3$) (7). Complex 7 is characterized by a mass spectrum showing the molecular peak at m/e = 570, and absorptions in the ^{1}H NMR spectra (Chart I) are compatible with the proposed structure.



(5)

Heating complex 7 to 70 °C in toluene caused dehydrogenative rearrangement (eq 5), and chromatography over Al$_2$O$_3$ (5% H$_2$O), eluting a yellow band, yielded the complex Cp*Ru(PPh$_3$)(OC$_4$H$_5$) (8) in 45% yield. The mass spectrum of 8 closely resembles that of 7 but is shifted by 2 mass units to lower molecular weights. Characteristic features in the ^{13}C and ^{1}H NMR spectra (Chart II) are a signal at 194 ppm (^{13}C) and a doublet at 9.0 ppm (^{1}H). The IR spectrum shows a carbonyl band at 1651 cm^{-1}. Other chemical shifts and couplings are in accord with a π-allyl ligand. The butenyloxy ligand, as can be observed in the mass spectrum already, has been dehydrogenated and transformed into a π-allenecarboxaldehyde group η^3 complexed to Ru.

Analogous reactions were found with olefins and acetylenes (eq 6). Ethylene and styrene required 50 °C for reaction; tolane readily reacted with 2 in toluene at ambient temperature. In neither case was an olefin addition product analogous to 7 isolated. Instead, the π-allenecarboxaldehyde complexes 9–11, which complete their coordination shell with 1 mol of olefin or acetylene, are formed directly. Mass spectral (see Experimental Section) and NMR data (Chart II) are all very similar to those of 8.



(6)

9 L = CH$_2$=CH$_2$
10 L = PhCH=CH$_2$
11 L = PhC≡CPh

Acrylic Acid Derivatives. A mode of coordination similar to the one shown by the butenyloxy group can be envisaged for an olefinic acid. Reaction of 1 with simple carboxylic acids (CH$_3$COOH), even at very low temperature, gave only dark-colored, oily, polymeric material. Acrylic acid, in contrast, reacted with 1 at –20 °C (eq 7),

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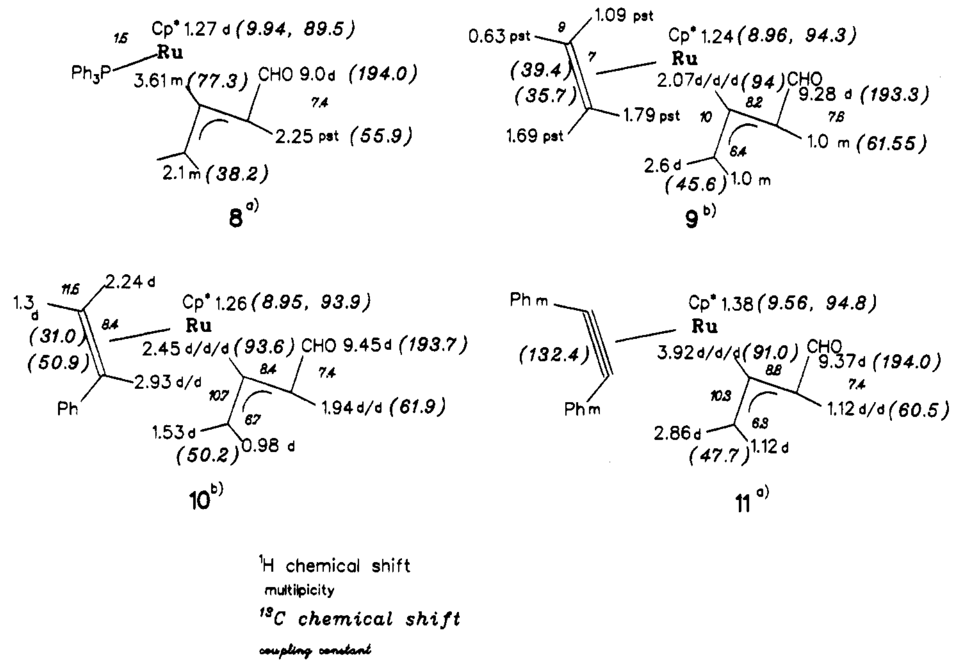
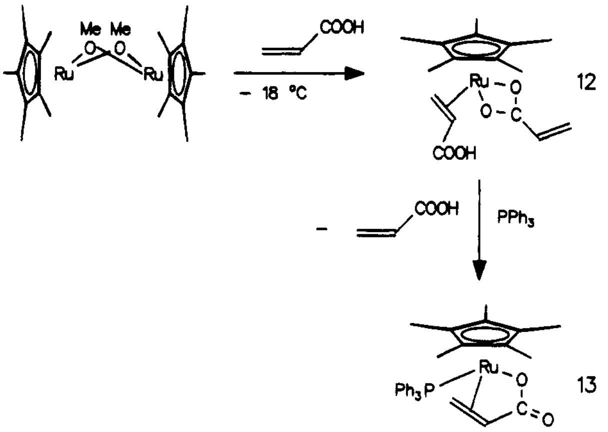
[10] Osakada, K.; Grohmann, A.; Yamamoto, A. *Organometallics* **1990**, *9*, 2092.

Chart II. NMR Parameters for Compounds 8–11

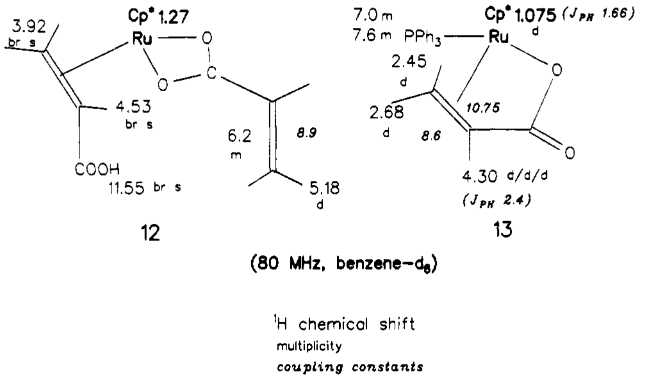


forming a red precipitate in very high yield, which could be crystallized from toluene/pentane.



(7)

Chart III. NMR Parameters for Compounds 12 and 13



The ${}^1H$ NMR spectrum of the compound (Chart III) shows two multiplets at 4.5 and 3.9 ppm and a broad signal with an intensity of one proton at 11.5 ppm, suggesting the presence of a free carboxylate group. Two broad peaks at 5.2 and 6.2 ppm are assigned to protons of an uncomplexed olefin. From the ratio of olefinic to Cp* protons two molecules of acrylic acid must be present in the monomeric complex, which is best accommodated by structure **12** with one acrylate bound in an η^2(O,C,O′) fashion and one acrylic acid coordinated only through the olefinic double bond as shown in eq 7. The relatively broad features of some protons, depending on the solvent, suggest an interchange of the two differently bound acrylic acids in more polar solvents.

Addition of PPh_3 to **12** causes coordination of the phosphine and loss of 1 mol of acrylic acid with possible isomerization of the carboxy group of the second mole into an η^3(O,C,C′) bonding mode in **13**. Adduct **13** has been identified through its ${}^1H$ NMR spectrum, showing an AMX pattern for the complexed olefinic protons (Chart III), where H_A at δ 4.30 and the Cp* signal are further split into doublets by coupling to phosphorus (splitting of the signal due to the occurrence of two diastereoisomers is less probable since it has not been observed in other proton signals). Bands at 1650 and 1635 cm^{-1} in the infrared spectrum are assigned to the carboxylate group. From pentane/toluene **13** crystallizes with $^1/_2$ mol of toluene, which is evident from the NMR spectrum of the crystals and is in accord with the elemental analysis.

Discussion

The formation and relative stability of the butenyloxy complex **2** as opposed to simple olefin adducts to **1**[1] must be traced back to the change in geometry of the Ru–O–Ru–O rhombus when **1** and **2** are compared. The unique stability of **1** as a coordinatively unsaturated 16-VE complex is best explained by specific π-bonding from filled oxygen into empty ruthenium orbitals. The Ru–O partial double-bond character is reflected in the relatively short Ru–O distances in **1** (2.055 (5), 2.057 (4) Å[4,5]). Recent kinetic results on phosphine exchange in the complexes $Cp^*Ru(PMe_3)_2X$,[11] where a particularly low activation enthalpy ΔH^* for X = OR was attributed to π-dative stabilization from oxygen lone pairs in the coordinatively unsaturated transition state $[Cp^*Ru(PMe_3)X]$, go in the same direction. Since oxygen π-bonding is into the d_{xz} or

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(11) Bryndza, H. E.; Domaille, P. J.; Paciello, R. A.; Bercaw, J. E. *Organometallics* **1989**, *8*, 379.

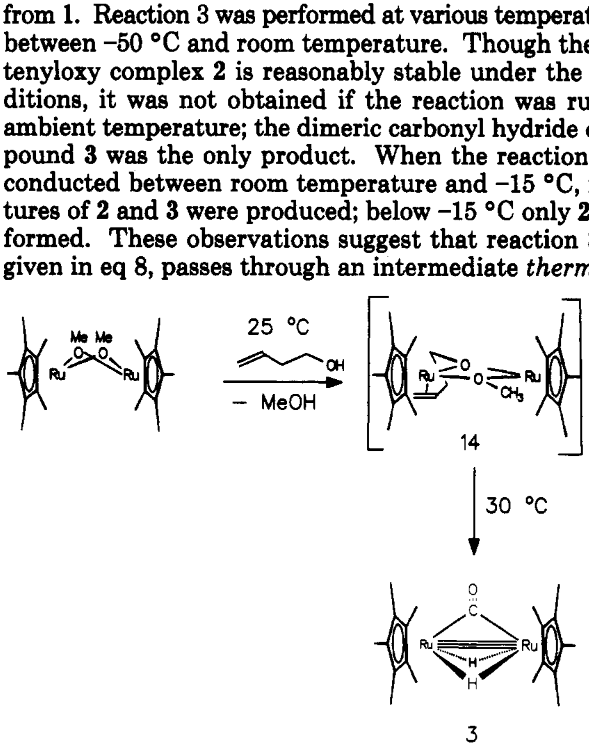
d_{yz} orbital (taking the z direction as the Ru to ring normal and the principal direction of the Ru d orbitals as governed by the strongest covalent interaction, that to the Cp ligand) of Ru and the Ru–O σ-bond is highly polar, the Ru atom in **1** is a relatively poor donor (low electron density in the t_{2g} descendant subset) and poor acceptor (relatively high electron density in the e_g descendants) toward olefins. Incorporation of an olefinic bond in **2** obviously counterbalances oxygen π-bonding. This effect is reflected in the geometrical distortion and in the increase in Ru–O distance from 2.05 to 2.16 Å (Table I) as one goes from **1** to **2**. Once the olefin is bound to Ru, the metal–oxygen bond becomes weak and the metal acts as a reasonably strong donor toward the olefin, as seen from the relatively short Ru–C (2.138 (10), 2.165 (10) Å) and the relatively long olefinic C–C distances (1.422 (15) Å) in **2**. A similar effect on the geometry of the Ru–O–Ru–O rhombus was observed with the stronger π-accepting CO group, which adds to the ethoxy derivative of **1**[5] in the same cis fashion as the double bonds in **2**. Note that simple olefins such as ethylene and propylene do not form stable addition products with **1** but invariably lead to products not containing a Ru–O bond.[1,8,9] This situation appears to be specific for alkoxides; the closely analogous Cp*RuCl moiety is well capable of forming stable complexes with either mono- or diolefins.[9,12,13] The delicate balance between bonding of an olefinic double bond and cleavage of the Ru–O bond is achieved in **2** only due to a chelate effect. This view of the bonding situation in Cp*Ru alkoxo complexes is borne out by the experiments presented above.

Thermolysis of **2** yields the dimeric hydrido carbonyl compound **3** as the main product along with some of the dimeric dicarbonyl species **6**. Attempts to monitor the thermal decomposition of **2** in toluene-d_8 by ^{1}H NMR spectroscopy showed the gradual decrease of signals due to the starting compound with concomitant growth of Cp* signals of the final products **3** and **6**. An initially growing and redisappearing hydride signal at −7 ppm indicates a terminal, nonbridging hydride as one possible intermediate. Although cleavage of the butenol C_α–C_β bond in **2** must have occurred to form **3** and **6**, no propene was found either in NMR experiments or by GC investigation of the mixture after reaction. This could be due to a reaction of liberated propene with **3** similar to what has been observed with the closely related tetrahydride Cp*Ru(μ-H)$_4$RuCp*.[14] Products formed in this way are anticipated to be unstable under the conditions, which could account for the relatively low yield of isolated complexes in this thermolysis reaction.

Given a combined yield for **3** and **6** of 60%, a detailed mechanism remains speculative but should principally follow the steps discussed previously for the formation of **3** from thermolysis of **1** or from its electrophilically or nucleophilically induced high-yield conversion.[7] The first mechanistic step is thought to be Ru–O bond cleavage followed by successive C–H and C–C bond activation in the bridging alkoxy ligand leading to the final products.

Note that thermolysis of **2** proceeds at a temperature well below the decomposition temperature of **1**, indicating a loss of stability through decreased Ru–O interaction which is not compensated by olefinic π-bonding in **2**. Alternatively stated, olefin coordination, as has been found in the reactions of **1** with monoolefins and cyclic polyolefins,[1,8,9] always weakens the Ru–O bond.

Similar reasoning can be applied to the formation of **2** from **1**. Reaction 3 was performed at various temperatures between −50 °C and room temperature. Though the butenyloxy complex **2** is reasonably stable under the conditions, it was not obtained if the reaction was run at ambient temperature; the dimeric carbonyl hydride compound **3** was the only product. When the reaction was conducted between room temperature and −15 °C, mixtures of **2** and **3** were produced; below −15 °C only **2** was formed. These observations suggest that reaction 3, as given in eq 8, passes through an intermediate *thermally less stable than the final product.* Conceivably this intermediate could be the methoxy–butenyloxy complex **14**, where complexation of *one* olefinic double bond distorts the geometry of the dimer such that the residual alkoxy bondings are greatly destabilized and undergo degradation under conditions milder than in the doubly olefin coordinated final product.



(8)

The same arguments can be applied to the less readily complexing alkenols 4-pentenol and the 3-hexenols. A double bond one position further from the alkoxo group as well as terminal alkyl substitution seems less suited for internal coordination and weakens π-bonding to an extent that a stable complex is not formed. The consequence is again C–H activative degradation leading to **3**. Note that these degradations with olefinic alcohols (eq 2) proceed under rather mild conditions, well below the reaction temperature of **1** with non-hydroxylic olefins. Accordingly, complex **3** is formed exclusively in rather high yield.

Dehydrogenation of the butenyloxy to an allenecarboxaldehyde ligand in the course of the reaction of **2** with phosphines, olefins, or acetylenes (reactions 5 and 6) is thought to proceed through the mononuclear cleavage product, analogous to **7**, isolated with triphenylphosphine. Cleavage of the dimer with olefins and acetylenes requires a somewhat higher temperature as in the case of the phosphine. The stronger electron accepting π-acids weaken the Ru–O bond such that β-elimination from the butenyloxy ligand, the initial step for the formation of **9**–**11**, proceeds at this same temperature leading to the allenecarboxaldehyde complex in one step.

Experiments on β-elimination at Pt–alkoxy complexes[15] had suggested that an available coordination site is a prerequisite for hydrogen migration to occur. While this may hold for many cases, in particular square-planar 16-electron d^8 complexes, in the above reactions we are faced with the puzzling fact that additional coordination of an olefinic double bond to a formerly coordinatively unsatu-

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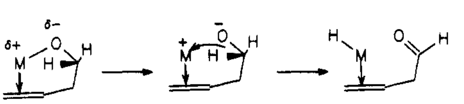
Scheme I. β-Elimination Mode of Polar, Destabilized Alkoxides



rated metal center does not *stabilize*, but *destabilizes* the latter toward β-elimination. This can be understood if in this particular case the initial step of the β-elimination is complete or partial heterolysis of the highly polar Ru–oxygen bond as indicated in Scheme I. Coordination of the olefinic double bond to 1 causes an increase in Ru–O bond polarity because of the lack of stabilizing oxygen to ruthenium π back-bonding, thus facilitating its cleavage.

Experimental Section

All experiments were conducted under nitrogen with absolute, nitrogen-saturated solvents using conventional Schlenk techniques. ^{1}H and ^{13}C NMR spectra were recorded on Bruker SY 80 and Varian Unity 300 and 500 spectrometers and IR spectra on a Perkin-Elmer 842 instrument. 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.

Bis[(η²(*C*=*C*)-μ₂(*O*)-but-3-en-1-yloxy)(pentamethylcyclopentadienyl)ruthenium] (2). To a solution of 0.26 g of 1 (0.49 mmol) in 30 mL of pentane cooled with an ice/salt mixture (−18 °C) was added 84 μL (0.97 mmol) of 3-buten-1-ol. After 2 h a red precipitate had formed. The solvent was evaporated to dryness under high vacuum; the residue was washed once with a small portion of pentane and subsequently extracted with several quantities of the same solvent. The filtered solution was concentrated to 20 mL and cooled to −50 °C, whence dark red rhombic crystals separated. The yield was 0.27 g (95%). For the NMR spectrum, see Chart I. MS (m/z; I_{rel}, %): 544 (85, M − C_4H_7OH), 470 (90, $(Cp^*Ru)_2$ − 4H), 308 (100, $Cp^*RuOC_4H_7$). Anal. Calcd for $C_{28}H_{44}O_2Ru_2$ (M_r 614.8): C, 54.70; H, 7.21. Found: C, 54.64; H, 7.38.

(η³-Butenyloxy-*O*,*C*,*C*′)(pentamethylcyclopentadienyl)(triphenylphosphine)ruthenium (7). An ether solution containing 0.2 g (0.66 mmol of Ru) of 2 and 0.17 g (0.66 mmol) of PPh_3 was stirred for 1 h at room temperature. When the color had turned from red to yellow, the solvent was evaporated in vacuo, the residue was extracted with several portions of pentane, and the filtered solution was concentrated to 20 mL. When this solution was cooled to −50 °C, the complex crystallized as dark yellow needles. The yield was 0.3 g (80%). For the NMR spectrum, see Chart I. MS (m/z; I_{rel}, %): 570 (20, M^+), 527 (55, M − C_3H_7), 499 (71, M − C_4H_7O), 279 (100, $Cp^*RuC_3H_7$). Anal. Calcd for $C_{32}H_{37}OPRu$ (M_r 569.7): C, 67.47; H, 6.55. Found: C, 67.65; H, 6.64.

(η³-1-Formylprop-2-en-3-yl-*C*,*C*′,*C*″)(pentamethylcyclopentadienyl)(triphenylphosphine)ruthenium (8). A solution of 0.13 g (0.77 mmol) of 7 in 20 mL of cyclohexane was heated for 6 h to 70 °C. The solution was evaporated, the residue was extracted with pentane, and the pentane extract was chromatographed over alumina (5% H_2O). A yellow band was eluted with toluene/ether (2:1). After the solvent was evaporated in vacuo, the residue was dissolved in pentane. The complex crystallized from the concentrated pentane solution at −15 °C as yellow needles. The yield was 0.2 g (45%). For the NMR spectrum, see Chart II. IR (KBr): 2708 (C*H*O), 1651 (CH*O*) cm^{-1}. MS (m/z; I_{rel}, %): 568 (16, M^+), 499 (100, Cp^*RuPPh_3), 306 (95, $Cp^*RuMC_4H_5O$). Anal. Calcd for $C_{32}H_{35}OPRu$ (M_r 567.7): C, 67.71; H, 6.21. Found: C, 67.50; H, 6.33.

(η²-Ethylene)(η³-1-formylprop-2-en-3-yl-*C*,*C*′,*C*″)(pentamethylcyclopentadienyl)ruthenium (9). In a pressure Schlenk tube was placed 0.14 g (0.54 mmol Ru) of 2 in 20 mL of toluene. The tube was pressurized with 2 bar of ethylene and the solution stirred at 40 °C for 2 h. After evaporation of the solvent workup was as described for compound 8 above. The yield after crystallization from pentane at −15 °C was 0.11 g (65%). For the NMR spectrum see Chart II. IR (KBr): 2720 (C*H*O), 1650 (CH*O*) cm^{-1}. MS (m/z; I_{rel}, %): 306 (67, M − C_2H_4), 278 (85, M − C_3H_4O), 236 (100, Cp^*Ru − H). Anal. Calcd for $C_{16}H_{24}ORu$ (M_r 333.4): C, 57.64; H, 7.25. Found: C, 55.14; H, 6.96.

Table II. Final Atomic Coordinates of 2

atom	x	y	z	U(eq), Å^2
Ru	0.79342 (1)	0.78752 (7)	0.0	0.033 (1)
O	0.7559 (1)	0.6107 (6)	0.0088 (5)	0.036 (3)
C11	0.7384 (2)	0.9993 (12)	0.0740 (7)	0.049 (6)
C12	0.6986 (3)	1.0058 (11)	0.0888 (8)	0.049 (6)
C13	0.6843 (3)	0.8508 (11)	0.0980 (7)	0.046 (5)
C14	0.7020 (3)	0.7321 (13)	0.1396 (7)	0.050 (6)
C1	0.8021 (2)	0.9296 (11)	−0.1204 (7)	0.042 (5)
C2	0.8202 (3)	0.9813 (11)	−0.0455 (7)	0.042 (5)
C3	0.8447 (3)	0.8678 (12)	−0.0227 (6)	0.049 (6)
C4	0.8391 (3)	0.7406 (11)	−0.0787 (7)	0.047 (5)
C5	0.8130 (3)	0.7839 (12)	−0.1405 (7)	0.048 (6)
C1′	0.7736 (3)	1.0216 (14)	−0.1643 (9)	0.072 (8)
C2′	0.8193 (3)	1.1389 (12)	−0.0117 (10)	0.063 (7)
C3′	0.8737 (3)	0.8889 (17)	0.0439 (9)	0.075 (8)
C4′	0.8609 (3)	0.6029 (15)	−0.0818 (10)	0.076 (8)
C5′	0.8023 (3)	0.6849 (15)	−0.2163 (8)	0.068 (7)

(η²-Stilbene)(η³-1-formylprop-2-en-3-yl-*C*,*C*′,*C*″)(pentamethylcyclopentadienyl)ruthenium (10). A solution of 0.2 g of 2 (0.72 mmol of Ru) and 65 μL (0.75 mmol) of styrene in 20 mL of toluene was heated for 3 h to 50 °C. The workup was as described above. The yield was 0.12 g (40%) of yellow needles from pentane. NMR spectrum, see Chart II. Due to rapid decomposition at 110 °C no mass spectrum could be obtained. Anal. Calcd for $C_{22}H_{28}ORu$ (M_r 409.5): C, 64.52; H, 6.89. Found: C, 64.57; H, 6.91.

(η²-1,2-Diphenylacetylene)(η³-1-formylprop-2-en-3-yl-*C*,*C*′,*C*″)(pentamethylcyclopentadienyl)ruthenium (11). The preparation was as described for compound 10 with a reaction time of 6 h at 40 °C. The yield was 0.21 g (90%) of red needles from diffusion of pentane into a concentrated toluene solution at −15 °C. For the NMR spectrum, see Chart II. IR (KBr): 2710 (C*H*O), 1653 (CH*O*) cm^{-1}. MS (m/z; I_{rel}, %): 484 (80, M^+), 455 (100, M − CHO), 314 (90, Cp^*RuPh), 236 (95, Cp^*Ru − H). Anal. Calcd for $C_{28}H_{30}ORu$ (M_r 483.6): C, 69.54; H, 6.25. Found: C, 69.50; H, 6.41.

(η²-Acrylato-*O*,*O*′)(η²-acrylic acid-*C*,*C*′)(pentamethylcyclopentadienyl)ruthenium (12). A pentane solution of 0.2 g (0.74 mmol of Ru) of 1 was cooled to −18 °C, and 75 μL of acrylic acid was added. After the mixture was stirred for 1 h at this temperature, a red solid had separated. The solvent was decanted, the red residue was extracted with toluene, and the extract was filtered and concentrated to 10 mL. Pentane was diffused into the toluene phase at −50 °C, which caused crystallization of 0.13 g (95%) of red plates. IR (KBr): 1650, 1169 (COO) cm^{-1}. Due to decomposition at elevated temperature, no mass spectrum could be obtained. Anal. Calcd for $C_{16}H_{22}O_4Ru$ (M_r 379.4): C, 50.65; H, 5.84. Found: C, 51.18; H, 6.18.

(η³-Acrylato-*O*,*C*′,*C*″)(pentamethylcyclopentadienyl)(triphenylphosphine)ruthenium (13). A 0.18-g (0.47-mmol) amount of 12 was stirred with 0.15 g (0.47 mmol) of triphenylphosphine in 30 mL of ether for 3 h at ambient temperature. After evaporation of the solvent the residue was extracted with toluene; the toluene solution was filtered and diluted with pentane. The product crystallized on cooling to −50 °C as yellow plates. The yield was 0.23 g (75%). IR (KBr): 1645 (COO) cm^{-1}. Due to decomposition at elevated temperature, no mass spectrum could be obtained. Anal. Calcd for 13·$^1/_2$(toluene), $C_{69}H_{74}O_4P_2Ru_2$: C, 67.30; H, 6.06. Found: C, 67.35; H, 5.91.

X-ray Diffraction Study of 2. A crystal fragment with dimensions 0.30 × 0.52 × 0.04 mm was sealed in a Lindemann glass capillary. X-ray data were collected on a Philips PW 1100 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at room temperature. A least-squares calculation with the diffractometer settings for 18 reflections gave the following parameters for the orthorhombic unit cell: a = 38.936 (8) Å, b = 8.976 (2) Å, c = 15.406 (3) Å. The space group from systematic extinctions, in accord with the structure solution, is *Fdd*2 (No. 43). With Z = 8 the calculated density for $C_{28}H_{44}O_2Ru_2$ (M_r 614.8) is 1.517 g/cm^3. Intensity data ($\theta/2\theta$ scans, θ_{max} = 25°) were collected for one octant. An Lp correction and in a later stage, i.e. after refinement of the structure with isotropic temperature factors, an empirical absorption correction (μ = 10.3 cm^{-1})[16] were applied. The structure was solved by the Patterson method. R indices after refinement with anisotropic temperature factors were R = 0.037 and $R_w(F)$ = 0.039. A total of 1225 independent reflections with $F_o \geq 2\sigma(F_o)$ was used in the calculations. Methyl hydrogen atoms could not be located, but the three hydrogen atoms of the ethylene part appeared in a final difference Fourier map. The SHELX program package was used for the calculations.[17]

For the space group *Fdd*2 one has to consider two polarities of the crystal structure. In view of the limited data set, we did not attempt to determine the polarity, however. Final atomic parameters are listed in Table II. Additional data (listings of anisotropic temperature factors, F_o/F_c listings, additional bond distances and angles) may be obtained from the Fachinformationszentrum, Ges. für technisch-wissenschaftl. Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany, by quoting CSD 55601, the names of the authors, and the journal.

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Supplementary Material Available: Tables of bond distances and angles, least-squares planes, and thermal parameters for 2 (3 pages). Ordering information is given on any current masthead page.

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Electrochemistry of Organosilicon Compounds. 3. Synthesis of Poly(disilanylene)ethylenes by Electrolysis of Bis(chlorosilyl)ethanes[1]

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Electrolysis of 1,2-bis(chloromethylphenylsilyl)ethane (**1**) and 1,2-bis[chloromethyl(*p*-tolyl)silyl]ethane (**6**) in 1,2-dimethoxyethane using copper as the electrodes and tetrabutylammonium tetraphenylborate as the supporting electrolyte afforded poly(disilanylene)ethylenes with high molecular weights, in which no silicon–oxygen bonds in the polymer backbone are included. The effect of supporting electrolytes and solvents on the silicon–silicon bond formation is discussed.

Introduction

In recent years, much interest has been focused on the chemistry of polymeric organosilicon compounds that have silicon–silicon bonds in the polymer backbone. In this field, the silicon–silicon bond formation is of considerable importance for building up these molecules. Many papers concerning studies on the formation of the Si–Si bond have been reported to date.[2–14]

Recently, we have demonstrated that the electrochemical reduction of chlorosilanes in an undivided cell is effective for the formation of silicon–silicon bonds and affords polysilane oligomers in high yields.[1a,b] In this paper, we wish to report that poly(disilanylene)ethylenes with high molecular weights can be obtained by the reduction of 1,2-bis(chlorosilyl)ethanes with the use of copper as the electrodes and tetrabutylammonium tetraphenylborate as the supporting electrolyte in 1,2-dimethoxyethane.

Results and Discussion

As described in the previous paper,[1b] lower homologues of polysilanes such as disilanes, trisilanes, tetrasilanes, and

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