Deactivation of the Grubbs Carbene Complex $[RuCl_2({=}CHPh)(PCy_3)_2]$ by Allylic Alcohols

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*Summary: While the (hydroxymethyl)carbene complex $[RuCl_2({=}CHCH_2OH)(PCy_3)_2]$ (**2**), prepared by metathesis from $[RuCl_2({=}CHPh)(PCy_3)_2]$ (**1**) and allyl alcohol, reacts in solution to give the carbonyl derivative $[RuCl_2(CO)(PCy_3)_2]$ (**3**), in the absence of solvent the methoxycarbene isomer $[RuCl_2({=}CHOCH_3)(PCy_3)_2]$ (**4**) is formed. The catalytic reaction of **1** with allyl alcohol affords, besides small amounts of ethene and acrolein, predominantly propionaldehyde; with 3-buten-2-ol and catalytic amounts of **1**, 3-butanone is obtained exclusively.*

In the course of investigations to apply the ruthenium-catalyzed olefin metathesis reaction to functionalized olefins, Grubbs and co-workers reported that the vinylcarbene complex $[Ru(O_2CCF_3)_2({=}CHCH{=}CPh_2)(PPh_3)_2]$ reacts with allyl ethyl ether, $CH_2{=}CHCH_2OEt$, to give the isomer $CH_3CH{=}CHOEt$ and the metathesis product $[Ru(O_2CCF_3)_2({=}CHOEt)(PPh_3)_2]$.[1] The ethoxycarbene complex, which has not been isolated, is rather labile and decomposes in CH_2Cl_2 to give mainly the carbonylruthenium(II) compounds $[Ru(O_2CCF_3)_2(CO)(PPh_3)_2]$ and $[RuH(O_2CCF_3)(CO)(PPh_3)_2]$, respectively.[1] The bis(tricyclohexylphosphine) counterpart $[RuCl_2({=}CHOEt)(PCy_3)_2]$ is more stable and has been obtained from $[RuCl_2({=}CHPh)(PCy_3)_2]$ (**1**) and ethyl vinyl ether in 66% yield.[2]

Recently, we found that the cationic (carbyne)hydridoruthenium complexes $[RuHCl({\equiv}CCH_3)(PCy_3)_2(L)]A$ (L = OEt_2, OH_2, NMe_2Ph; A = BF_4, $B(C_6F_5)_4$, etc.), generated from the hydrido vinylidene precursor $[RuHCl({=}C{=}CH_2)(PCy_3)_2]$ and acids HA, are efficient catalysts for cross-olefin metathesis of cyclopentene with methyl acrylate.[3] If, instead of $CH_2{=}CHCO_2Me$, allyl alcohol ($CH_2{=}CHCH_2OH$) was used, the efficiency dropped and, in addition to traces of $CH_2{=}(CHCH_2CH_2CH_2CH)_3{=}CHCH_2OH$, only small quantities of the lower homologues $CH_2{=}CHCH_2CH_2CH_2CH{=}CHCH_2OH$ and $CH_2{=}(CHCH_2CH_2CH_2CH)_2{=}CHCH_2OH$ in the molar ratio of ca. 8:1 were obtained.[4] It appeared that in the presence of allyl alcohol the catalyst decomposed to give (catalytically inactive) carbonylruthenium compounds similar to those already observed by Grubb's group.[2]

To learn more about the behavior of allylic alcohols toward ruthenium complexes used as catalysts in olefin metathesis processes, the reactivity of Grubbs-type ruthenium carbenes $[RuCl_2({=}CHR)(PCy_3)_2]$ toward $CH_2{=}CHCH_2OH$ and $CH_2{=}CHCH(OH)CH_3$ was investigated. Treating **1** with a 10-fold excess of allyl alcohol led, after a short period of time, to the formation of the expected (hydroxymethyl)carbene derivative **2**, formed by metathesis (Scheme 1). Typical spectroscopic features of **2** (which is a violet, moderately air-stable solid) are the low-field resonance at δ 18.92 for the carbene CH proton and the triplet at δ 5.61 for the OH proton in the ^1H NMR spectrum. The splitting of the OH signal, being due to $^1H-^1H$ coupling, is noteworthy insofar as in the ^1H NMR spectrum of the related compound $[RuCl_2\{{=}CH(CH_2)_3OH\}(PCy_3)_2]$ a broad singlet has been observed.[5] The spectrum of **2** in $CDCl_3$ in the presence of D_2O does not display a resonance at δ 5.61, which is consistent with the given assignment.

In contrast to **1**, compound **2** is unstable in solution. If the decomposition process is monitored by ^{31}P NMR spectroscopy in CH_2Cl_2, the disappearance of the singlet of **2** at δ 38.5 is accompanied by the appearance of a new signal at δ 35.1, which by comparison can be assigned to the carbonyl complex **3**.[6] The IR spectrum of the decomposition product **3** and that of an authentic sample were also identical. Regarding the mechanism of the conversion of **2** to **3** (see Scheme 2), we assume that in the initial step a β-H shift from the CH_2 carbon to the metal atom occurs to give intermediate **A**. Intramolecular reductive elimination would then generate the π-enol derivative **B**, which could undergo an isomerization to afford **C**. Upon oxidative addition of the C−H bond of the aldehyde to the metal center, the (acyl)hydridoruthenium(II) species **D** could be formed, which reacts by methyl migration and methane elimination to yield **3**. There is ample evidence for the metal-assisted decarbonylation of aldehydes RCHO to give CO and RH, with rhodium and ruthenium compounds playing an important role.[7]

The most surprising result, however, is that for complex **2** two pathways for deactivation exist, depending on whether the reaction takes place in solution or without a solvent. If a solid sample of **2** is stored under argon at room temperature for 2−3 days, the ^{31}P NMR spectrum of the substance shows, besides the singlet for

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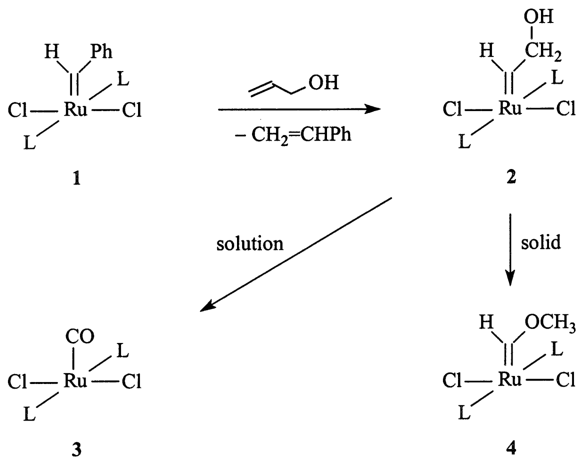
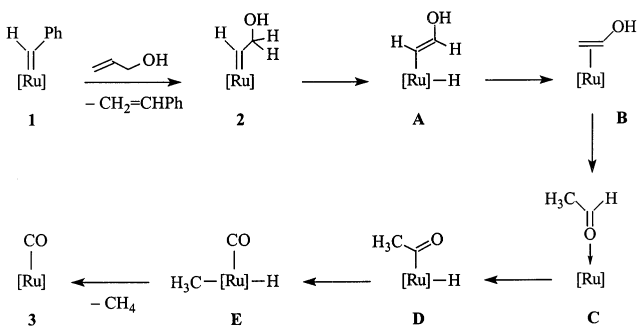
Scheme 1[a]



[a] L = PCy_3.

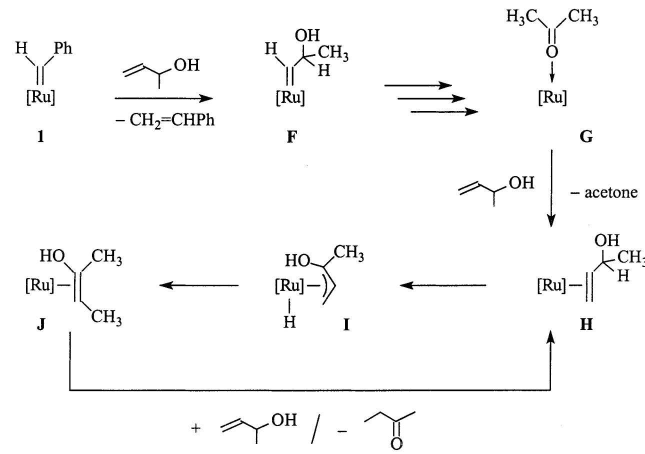
Scheme 2[a]



[a] [Ru] = $RuCl_2(PCy_3)_2$.

2, a new resonance at δ 27.6 which is shifted by 7.5 ppm to higher field compared with **3** and assigned to the methoxycarbene compound **4** (see Scheme 1). Storing a solid sample of **2** under argon for 6 h at 60 °C leads to a complete rearrangement of **2** to **4**. In contrast to **2**, the ^1H NMR spectrum of **4** displays the signal for the carbene CH proton at δ 13.94, which is at a position similar to that found for $[RuCl_2({=}CHOEt)(PCy_3)_2]$.[2] In the ^{13}C NMR spectrum of **4** the resonance for the carbene carbon atom appears at δ 297.1, the chemical shift being in agreement with $[RuCl_2({=}CHOEt)(PCy_3)_2]$ and that of other Fischer-type carbenes with a d^6 metal center.[8] A possible explanation for the course of the isomerization from **2** to **4** is that a nucleophilic attack of the hydroxy group of the CH_2OH moiety at the carbene carbon atom occurs, which would lead to a protonated oxirane with a negatively charged $[RuCl_2(PCy_3)_2]$ unit as a substituent at the three-membered ring. After the $CH{-}CH_2$ bond of the ring is broken and proton transfer from oxygen to the CH_2 carbon atom occurs, the $CH(OCH_3)$ ligand could be formed. Since the isomerization takes place only in the condensed phase, we cannot exclude that a bimolecular mechanism operates and that a hydroxy group of one molecule attacks the carbene carbon atom of the next. In this context it should be mentioned that we have previously described a series of reactions of organorhodium and -ruthenium complexes which also yield different products, depending on whether they proceed in solution or in the absence of a solvent.[9] A microreview on structural isomerization reactions in confined environments has recently appeared.[10]

Scheme 3[a]



[a] [Ru] = $RuCl_2(PCy_3)_2$.

The catalytic reaction of the Grubbs-type carbene **1** with $CH_2{=}CHCH_2OH$ in the molar ratio of ca. 1:1000 leads not only to a rapid consumption of **1** but also to a smooth isomerization of allyl alcohol to propionaldehyde. Small amounts of ethene and acrolein were also detected. If, instead of $CH_2{=}CHCH_2OH$, the corresponding methyl derivative $CH_2{=}CHCH(CH_3)OH$ is used, a clean conversion to 3-butanone takes place. The proposed mechanism for this reaction is shown in Scheme 3. While the first steps are probably quite similar to those for the decomposition of **2** to give **3**, the acetone adduct **G** cannot undergo (in contrast to intermediate **C** shown in Scheme 2) an oxidative addition and therefore reacts with the unsaturated alcohol to generate π-complex **H**. Subsequent β-H elimination yields the π-allyl hydrido derivative **I**, which could rearrange to the π-enol compound **J**. Replacement of the enol by 3-buten-2-ol to regenerate the catalytically active species **H** is probably accompanied by a rapid tautomerization of the enol to give the ketone $CH_3CH_2C(O)CH_3$, which is the only organic product detected in the reaction.

In summarizing, we observed that two distinct pathways for the conversion of the thermally labile hydroxymethylcarbene complex **2** exist. Moreover, we note that apart from compound **4**, generated by isomerization of **2** in the condensed phase, and the ethoxycarbene analogue $[RuCl_2({=}CHOEt)(PCy_3)_2]$, recently reported by Louie and Grubbs,[2] complexes of the general composition $[M({=}CHOR)(L)_n]$ are quite rare.[11] The main reason is that in general they cannot be prepared by following the Fischer methodology, since the primary intermedi-

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ate formed on this route with a metal−formyl bond is usually unstable.

Experimental Section

All operations were carried out under argon using standard Schlenk techniques. The starting material **1**[5] was prepared as described in the literature. NMR spectra were recorded on Bruker AC 200 and AMX 400 instruments. Abbreviations used: s, singlet; t, triplet; vt, virtual triplet; m, multiplet; br, broadened signal. GC/MS measurements were carried out using a Hewlett-Packard GCD instrument.

Preparation of $[RuCl_2(=CHCH_2OH)(PCy_3)_2]$ (2). A solution of **1** (123 mg, 0.15 mmol) in CH_2Cl_2 (10 mL) was treated with allyl alcohol (100 μL, 1.47 mmol) and stirred for 15 min at room temperature. The volatile materials were evaporated in vacuo, and the oily residue was layered with acetone (3 mL). While the mixture was stored at 0 °C, a violet solid precipitated, which was separated from the mother liquor, washed twice with pentane (0 °C), and dried: yield 103 mg (88%); mp 55 °C dec. Anal. Calcd for $C_{38}H_{70}Cl_2OP_2Ru$: C, 58.75; H, 9.03. Found: C, 58.71; H, 9.17. ^{1}H NMR (200 MHz, $CDCl_3$): δ 18.92 (br s, 1H, $=CHCH_2OH$), 5.61 (t, J(H,H) = 4.6 Hz, 1H, CH_2OH), 3.92 (m, 2H, CH_2OH), 2.56−1.23 (br m, 66H, C_6H_{11}). ^{31}P NMR (81.0 MHz, $CDCl_3$): δ 38.5 (s).

Formation of $[RuCl_2(CO)(PCy_3)_2]$ (3) from 2. A solution of **2** (17 mg, 0.02 mmol) was dissolved in $CDCl_3$ (0.4 mL) in an NMR tube. After the solution was stored for 4 h at room temperature, the IR and ^{31}P NMR spectra revealed that the carbonyl complex **3** was exclusively formed. It was identified by comparison with data from the literature.[6]

Preparation of $[RuCl_2(=CHOCH_3)(PCy_3)_2]$ (4). A solid sample of **2** (116 mg, 0.15 mmol) was stored under argon for 6 h at 60 °C. After the material was cooled to room temperature, the violet solid was washed twice with acetone (2 mL each, 0 °C) and ether (2 mL) and dried: yield 115 mg (99%); mp 58 °C dec. Anal. Calcd for $C_{38}H_{70}Cl_2OP_2Ru$: C, 58.75; H, 9.03. Found: C, 59.16; H, 9.32. ^{1}H NMR (400 MHz, C_6D_6): δ 13.94 (s, 1H, $=CHOCH_3$), 2.97 (s, 3H, OCH_3), 2.88−0.89 (br m, 66H, C_6H_{11}). ^{13}C NMR (100.6 MHz, C_6D_6): δ 297.1 (br s, $=CHOCH_3$), 45.0 (s, $=CHOCH_3$), 33.4 (vt, N = 17.6 Hz, *ipso*-C of C_6H_{11}), 30.4, 27.0 (both s, C_6H_{11}), 28.1 (vt, N = 8.8 Hz; C2 and C6 of C_6H_{11}). ^{31}P NMR (162.0 MHz, C_6D_6): 27.6 (s).

Reaction of 1 with Allyl Alcohol in the Molar Ratio of 1:1000. A solution of **1** (120 mg, 0.15 mmol) in CH_2Cl_2 (5 mL) was treated at −78 °C with allyl alcohol (10 mL, 0.15 mol). After the solution was warmed to room temperature, it was stirred for 2 h. A change of color from red to yellow occurred. A sample of the gas phase was taken with a syringe, dissolved in C_6D_6, and investigated by ^{1}H NMR spectroscopy. Ethene was clearly detected. The volatile materials of the reaction mixture were condensed in a Schlenk tube, and the composition was studied by GC/MS. In addition to CH_2Cl_2 and small amounts of both allyl alcohol and acrolein, only propionaldehyde, CH_3CH_2CHO, was found: yield ca. 95%.

Reaction of 1 with Excess 3-Buten-2-ol. (a) A solution of **1** (105 mg, 0.13 mmol) in CH_2Cl_2 (5 mL) was treated with 3-buten-2-ol (0.8 mL, 9.20 mmol) and stirred for 10 min at room temperature. A stepwise change of color from violet to red and subsequently to pale brown occurred. The solution was concentrated in vacuo to ca. 1 mL, and pentane (5 mL) was added. A brownish solid precipitated, which in solution smoothly decomposed. It could not be characterized analytically. If the solid was dissolved in CH_2Cl_2 (2 mL) and the solution was treated with excess 3-buten-2-ol (1 mL), an isomerization to 2-butanone took place.

(b) In an NMR tube a solution of **1** (39 mg, 0.05 mmol) in CD_2Cl_2 (1 mL) was treated with an equimolar amount of 3-buten-2-ol (4.1 μL, 0.05 mmol). After the solution was stored for 1 min, the ^{1}H NMR spectrum indicated the formation of styrene and acetone. An excess of 3-buten-2-ol (50 μL, 0.58 mmol) was then added and the solution stored for 15 min. Both the ^{1}H and ^{31}P NMR spectra confirmed that the starting material **1** was consumed. The substrate 3-buten-2-ol was completely converted to 2-butanone. After a second sample of 3-buten-2-ol (50 μL, 0.58 mmol) was added to the solution, the ^{1}H NMR spectrum revealed that in ca. 15 min it was also converted to the isomeric ketone.

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