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η^1-Allyl Ligands

First X-Ray Structure Analyses of Rhodium(III) η^1-Allyl Complexes and a Mechanism for Allylic Isomerization Reactions**

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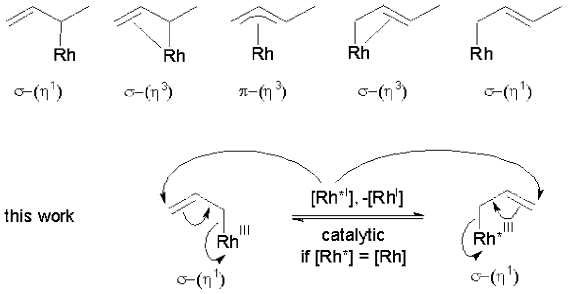
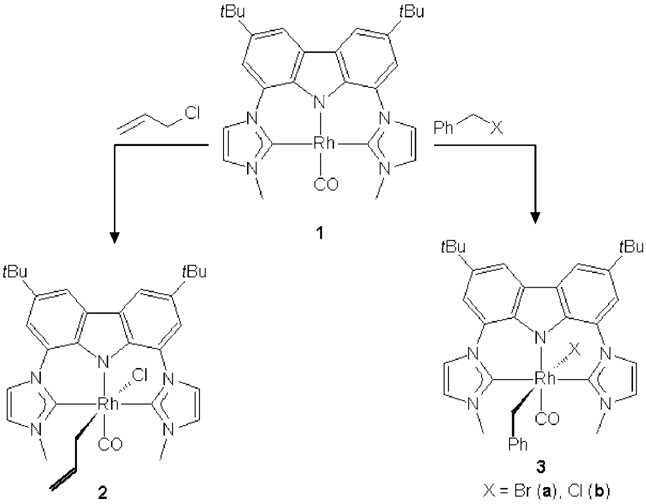
Dedicated to Professor Werner Tochtermann on the occasion of his 75th birthday

The allylic alkylation is an important reaction in organic synthesis and is catalyzed by a variety of different transition-metal complexes.[1] The regioselectivity of this reaction depends on the kind of metal as well as on the ligand. After oxidative addition of the allyl fragment to the catalyst, especially in palladium-catalyzed variants, an η^3-allyl fragment is considered to be the reactive intermediate that is subject to η^3–η^1–η^3 rearrangement reactions.[2] The rhodium-catalyzed[3–6] and iron-catalyzed[7] allylic alkylation has drawn attention because in many cases the *ipso*-substitution product was found to be the major isomer. A possible explanation for the regioselectivity and the enantioselectivity transfer would be a σ-allyl intermediate with a weak π-coordination (Scheme 1, top). A decrease in enantioselectivity is considered to occur via η^1-coordination so that rotation about the Rh−C bond is enabled and a decrease in regioselectivity is explained by a σ–π–σ isomerization.[7a] However, a structurally characterized Rh(η^1-allyl) complex has never been reported, although NMR spectroscopic analyses of such species are known.[8]



Scheme 1. Two different possible pathways for the isomerization of allyl ligands. In addition to the established σ-π-σ mechanism including an η^3-intermediate (top), isomerization can also be metal catalyzed (bottom).

Recently, we reported the highly nucleophilic Rh^I carbonyl complex **1** that bears a carbazol-based pincer ligand (bimca) that contains two N-heterocyclic carbene moieties.[9] Owing to the strong electron-donating properties of the bimca ligand the oxidative addition (mechanistically S_N2) of methyl iodide proceeds extremely fast.



Scheme 2. Reaction of complex **1** with allyl halides and benzyl halides leads to complexes **2** and **3a**,**b** with η^1-coordination.

To further characterize the reactivity of this complex we investigated its reactivity towards allyl halides. Complex **1** reacts with allyl chloride or benzyl bromide within 0.5 h at room temperature to the respective Rh^{III} allyl complex **2** and the Rh^{III} benzyl complex **3a** (Scheme 2). The reaction with benzyl chloride is much slower, suggesting an S_N2' mechanism for the reaction of allyl halides and an S_N2 mechanism for the reaction of benzyl halides. The ^{1}H NMR spectrum of the Rh allyl complex **2** clearly shows signals that are typical for a η^1-binding mode of the allyl moiety: a multiplet at $\delta = 5.09$ ppm (1 H) and two doublets at $\delta = 4.10$ (1 H) and 4.02 ppm (1 H) with $^3J_{HH}$ coupling constants of 10.0 Hz (*cis*) and 16.5 Hz (*trans*) for the protons of the double bond. The signal of the methylene protons at $\delta = 1.58$ ppm (2 H) is hidden by the *t*Bu signal, but could be identified by a ^{1}H,^{13}C NMR correlation experiment. In the spectrum run in CD_3CN the signals are separated, the methylene signal appears as a doublet of doublets at $\delta = 1.59$ ppm with a $^2J_{RhH} = 2.5$ Hz and $^3J_{HH} =$

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8.5 Hz. In the ^{13}C NMR spectrum the signal for the methylene carbon is at $\delta = 21.8$ ppm with $^{1}J_{\mathrm{RhC}} = 19.4$ Hz, and two singlets at $\delta = 118.9$ and 145.5 ppm for the carbon atoms of the double bond are characteristic of the η^1-binding mode of the allyl substituent.[10] The X-ray structure analysis of complex **2** confirms this rare coordination mode of the allyl ligand (Figure 1, left) and is the first molecular structure of a Rh η^1-allyl complex.[11] However, the quality of the structure analysis is rather low and thus a discussion of the bond lengths is not possible.

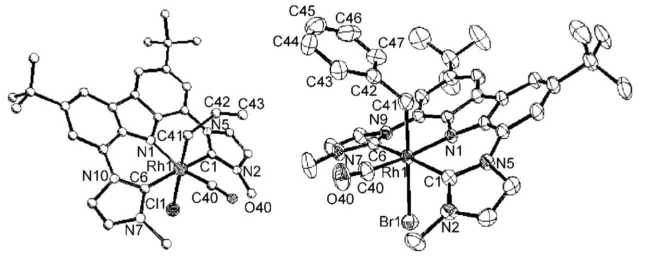
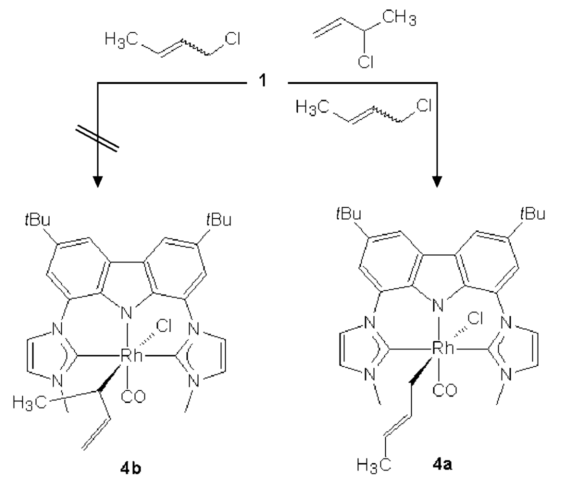


Figure 1. Molecular structures of the η^1-allyl complex **2** (left) and the η^1-benzyl complex **3a** (right). Selected bond lengths [Å] and angles [°] for complex **3a**: Rh1–Br1 2.6827(5), Rh1–C1 2.068(3), Rh1–C6 2.083(3), Rh–C40 1.855(4), C40–O40 1.138(4), Rh1–C41 2.120(4), C41–C42 1.480(5), C42–C43 1.387(5), C43–C44 1.393(7), C44–C45 1.367(8), C45–C46 1.357(8), C46–C47 1.377(6), C42–C47 1.384(5); Rh1-C40-O40 171.3(4), N2-C1-N5 103.9(3), N7-C6-N9 103.6(3).

The η^1-coordination mode is also preferred in the Rh benzyl complex **3a** and can be derived from the ^{1}H NMR spectrum showing a broad singlet for the methylene protons at $\delta = 2.51$ ppm, one doublet at $\delta = 5.98$ ppm (*o*-Ph), and two triplets at $\delta = 6.53$ (*m*-Ph) and 6.70 (*p*-Ph) ppm with a coupling constant of 7.4 Hz each. This assignment is confirmed in the ^{13}C NMR spectrum by the methylene carbon signal at $\delta = 24.4$ ppm with a direct Rh–C coupling constant of 20.4 Hz. Evidence for the η^1-benzyl coordination mode was also obtained from an X-ray structure analysis (Figure 1, right).[11] The molecular structure of benzyl complex **3a** shows the octahedrally coordinated Rh center with the benzyl and bromo ligand in *trans* positions. The benzyl ring is oriented toward one side of the molecule, indicating that rotation about the Rh−C bond should not be hindered in solution. The Rh1−C41 distance is 2.120(4) Å which is a typical value for a Rh−C(sp^3) bond. The C41−C42 bond measures 1.480(5) Å which is characteristic for a C(sp^3)−C(sp^2) bond clearly indicating no η^3-allyl mesomeric influence. The π-system in the aromatic ring is delocalized with typical bond lengths between 1.357(8) and 1.393(7) Å. The carbonyl ligand is bent out of the bimca ligand plane in the direction of the benzyl ligand (N1-Rh-C40 = 170.32(14)° and Rh-C40-O40 = 171.2(4)°).

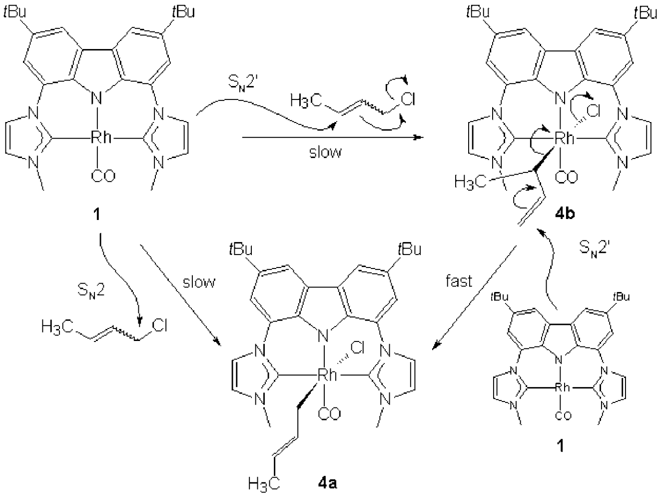
Upon heating complex **2** to 75 °C for 5 h neither CO dissociation to give an η^3-allyl complex nor CO insertion into the Rh-σ-allyl bond was found.

Owing to the exclusive η^1-coordination mode we expected 3-chloro-1-butene to react with **1** to give solely the η^1-allyl complex **4a** with an internal double bond, whereas 1-chloro-2-butene (crotyl chloride) should lead to complex **4b** bearing the η^1-allyl ligand with a terminal double bond (Scheme 3).



Scheme 3. Reaction of complex **1** with 3-chloro-1-butene as well as with 1-chloro-2-butene leads only to formation of complex **4a**.

With 3-chloro-1-butene the expected complex **4a** is formed, clearly by an S_N2' reaction. The double bond shows an *E*/*Z* ratio of (5:1). However, upon reaction of **1** with 1-chloro-2-butene, exclusively formation of complex **4a** occurred again, also in an *E*/*Z* ratio of 5:1 (1-chloro-2-butene was used as an *E*/*Z* mixture of 5:1). Formation of the expected complex **4b** with a terminal allyl double bond was not observed. To explain this result three different pathways can be envisaged. The first is dissociation of the CO ligand and formation of a η^3-allyl isomer, isomerization to the η^1-isomer, and reassociation of the CO ligand. However, as the η^3-isomer was never found upon irradiation with light or at elevated temperatures, this possibility is rather unlikely. Another possibility would be that 1-chloro-2-butene reacts by an S_N2 mechanism instead of the allylic S_N2' mechanism (see Scheme 4). Indeed, the



Scheme 4. Possible pathways for the formation of the η^1-allyl complex **4a** by either an S_N2 mechanism or a twofold S_N2' reaction via **4b**.

reaction with 1-chloro-2-butene is slower than that with 3-chloro-1-butene, however this decrease is expected for the reaction of an internal versus a terminal allylic double bond, a result of steric as well as electronic reasons. But the reaction is still faster than that of benzylchloride with complex **1**, which is an S_N2 reaction. In a typical S_N2 reaction benzylchloride should react three times faster than allylchloride.[12] We therefore envisaged that the highly nucleophilic [Rh(bimca)(CO)] complex **1** could react with the in situ formed η^1-allyl complex **4b** in an S_N2' fashion, so that the thermodynamically favored product **4a** with an internal double bond is formed.

To probe this third possibility we prepared [Rh(bimca^{Et})CO] complex **5**[11] that contains N-ethyl instead of N-methyl substituents at the imidazolinylidene moieties to conduct a cross-over experiment. This complex was converted into the η^1-allyl complex **6** by reaction with allylchloride. The reaction proceeded as smoothly as in the case of complex **2**. We could not only confirm the η^1-coordination mode of the allyl ligand by NMR spectroscopy (signal at $\delta = 1.67$ (superposed with ethyl signal), two doublets at $\delta = 4.06$ ($^3J_{HH} = 16.8$ Hz) and $\delta = 4.14$ ($^3J_{HH} = 9.9$ Hz) and a multiplet at $\delta = 5.18$ ppm), but we were also able to obtain an X-ray structure that confirms the exclusive η^1-allyl coordination mode (Figure 2).[11] The Rh–C41 bond is 2.132(2) Å and the σ-allyl moiety consists unambiguously of a single bond 1.475(4) Å (C41–C42) and a double bond 1.319(5) Å (C42–C43). The allyl moiety is not symmetrically oriented but pointing towards one side of the complex as observed in the allyl and benzyl complexes **2** and **3a**.

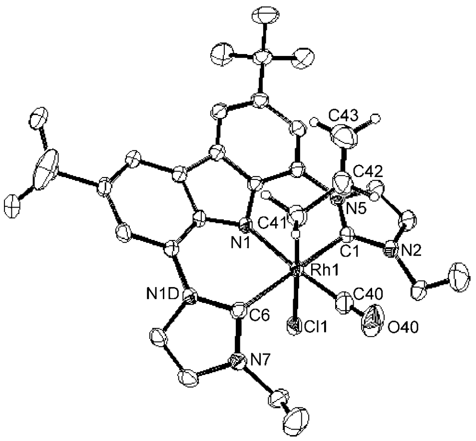
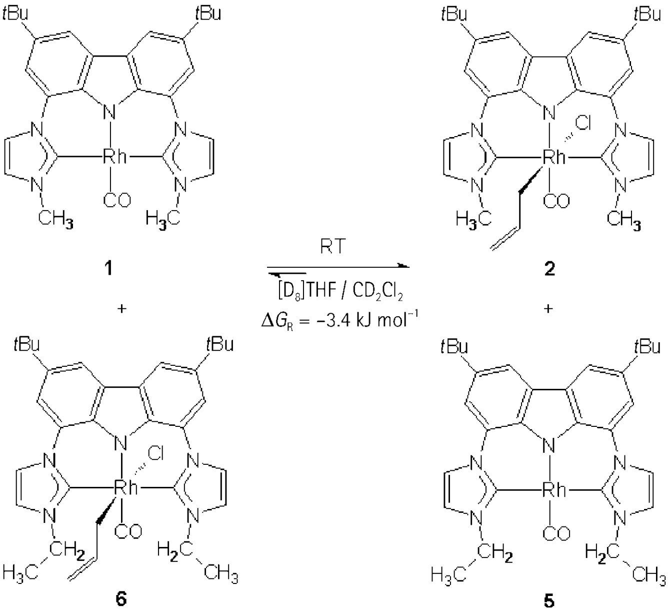


Figure 2. Molecular structure of the η^1-allyl complex **6**. Selected bond lengths [Å] and angles [°]: Rh1–Cl1 2.5463(6), Rh1–C1 2.082(2), Rh1–C6 2.075(2), Rh1–C40 1.851(3), C40–O40 1.137(3), Rh1–C41 2.132(2), C41–C42 1.475(4), C42–C43 1.319(5); N1-Rh1-C40 167.66(10), Rh1-C40-O40 170.8(3), N2-C1-N5 103.47(19), N7-C6-N10 103.73(19).



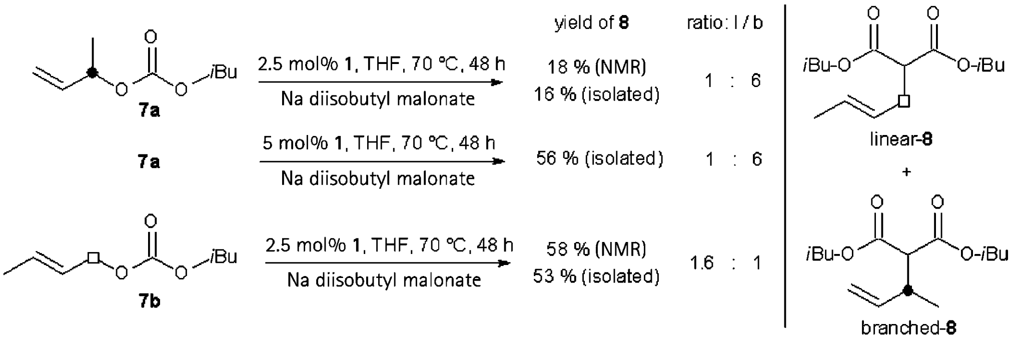
Scheme 5. Cross-over reaction experiment between the Rh^I complex **1** and the Rh^{III} complex **6** shows formation of complex **2** and **5** by transfer of the allyl ligand from **6** to **1**. Starting from the complexes **2** and **5** the identical ratio of **1**:**6**:**2**:**5** is formed, indicating a fast equilibrium of this reaction.

The cross reaction experiment was conducted by addition of one equivalent of **1** to a solution of complex **6** in [D$_8$]THF/CD_2Cl_2 (3:2; Scheme 5). After 30 min the ^1H NMR spectrum shows the signals of complexes **1**:**6**:**2**:**5** in a 1:1:2:2 ratio. This means that 2/3 of the η^1-allyl ligand was transferred from **6** to complex **1** under formation of **2** and complex **5**. After 5 h the ratio of the reaction mixture has not changed. To probe this thermodynamic equilibrium ratio we also treated complex **2** with one equivalent of **5**. The NMR spectrum shows formation of **1** and complex **6** in the same equilibrium ratio of 1:1:2:2 for **1**:**6**:**2**:**5**.

DFT calculations confirm[13] the higher stability of the products **2** and **5** with a reaction energy of $\Delta G_R(\text{theor}) = -8.6\,\text{kJ mol}^{-1}$ which is in good agreement with the experimental value of $\Delta G_R = -3.4\,\text{kJ mol}^{-1}$ (Scheme 5) within the error of precision. The theoretical results give an equilibrium constant of $K = 32$ and a ratio for **1**:**6**:**2**:**5** of 1:1:5.7:5.7, again supporting the experimental results.

Our results show that the η^1-allyl to η^1-allyl isomerization does not necessarily have to proceed via a η^3-allyl intermediate in the rhodium-catalyzed allylic alkylation (Scheme 1, top). An intermolecular pathway following an S_N2' metal-transfer reaction[14] can occur if the intermediate contains a terminal allyl double bond (Scheme 1, bottom). This finding could have important consequences for the regioselectivity of the rhodium- and iron-catalyzed allylic substitution reactions. As the isomerization could proceed faster than the oxidative addition of the allylic substrate, some free catalyst could induce the isomerization via an S_N2'-reaction. This situation would imply that the isomerization is dependent on the catalyst concentration.

To test whether complex **1** is an active catalyst in the allylic alkylation, we treated (3-buten-2-yl)isobutylcarbonate with 2 equivalents of sodium diisobutylmalonate in the presence of 2.5 mol% of complex **1** in THF at 70 °C for 48 h (Scheme 6). The isolated product **8** (16% yield) showed linear and the branched alkylation in the expected 1:6 ratio (with



Scheme 6. Reaction of branched (**7a**) and linear (**7b**) allyl carbonates with sodium diisobutylmalonate using complex **1** as a catalyst. For **7b** more isomerization occurs because a terminal η^1-allyl intermediate is formed which can undergo an S_N2' metal-transfer isomerization.

5 mol% **1**, the yield was 56%, and the ratio still 1:6). Reaction of the (2-buten-1-yl)isobutylcarbonate under identical conditions leads to product **8** with a linear:branched ratio of 1.6:1 in 53% yield. As expected for rhodium-catalyzed alkylation, mainly the *ipso* product is formed, however quite a large amount of the isomeric branched product was also formed, which could result from the S_N2' metal-transfer isomerization discussed above.

To evaluate if under catalytic conditions (small concentration of the catalyst, high concentration of the nucleophile) a nucleophilic attack is reasonable, we compared the reactivity of complex **1** towards complex **6** with the reactivity of sodium dimethylmalonate towards complex **6** in a stoichiometric reaction at concentrations that are typically applied in catalysis (0.5–2.5×10^{-2} mol L^{-1}). Reaction of complex **1** with the allyl complex **6** at room temperature showed that at concentrations of 2.5×10^{-2} mol L^{-1} the reaction is too fast to be monitored by NMR spectroscopy. At concentrations of 1.0×10^{-2} mol L^{-1} the equilibrium concentration is reached after 8 min and at 0.5×10^{-2} mol L^{-1} after about 18 min. Reaction of complex **6** with sodium dimethylmalonate at 0.5×10^{-2} mol L^{-1} immediately leads to a still unknown intermediate[15] that is only slowly converted into complex **5** and the allylic alkylation product (60% **5**, 40% alkylation product after 60 min). Although we were not able to characterize the intermediate further we expect it to be a cationic complex formed by release of sodium chloride. Under catalytic conditions in which allylcarbonates are used instead of allylchloride it is expected that the corresponding (electrophilic) cationic intermediate is formed more slowly (if at all). Therefore the malonate attack at the double bond is also expected to occur more slowly under catalytic conditions. Despite these differences between catalytic and stoichiometric conditions our results qualitatively show that metal complex **1** is indeed a better nucleophile than sodium malonate. Therefore an S_N2' metal-transfer reaction to form the thermodynamically most stable η^1-allyl intermediate is a reasonable explanation for the isomerization reaction in the rhodium-catalyzed allylic alkylation which proceeds without the formation of an η^3-allyl intermediate.

In conclusion we have shown the first X-ray crystal structures of rhodium η^1-allyl complexes. The formation of allyl complex **4a** (with an internal double bond) instead of **4b** (with a terminal double bond) from the reaction of 1-chloro-3-butene with **1** can be explained by a subsequent S_N2' metal-transfer reaction. The possibility of such a pathway was investigated by a cross-over experiment. These findings could have consequences for isomerization in rhodium-catalyzed allylic alkylation reactions for which complex **1** is a catalyst. More detailed kinetic studies concerning the stereochemical course and to quantify this isomerization reaction are our current efforts and will be reported in due course.

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[10] In contrast to Ref. [8a], but in accordance with Ref. [8b], the assignment of the ^{13}C NMR signals for the double bond is: $\delta =$ 118.9 (C15) and 145.5 ppm (C14) which was confirmed by ^{1}H,^{13}C NMR correlation experiments and is identical to the assignment of organic allyl double bonds.

[11] CCDC 711848 (**2**), CCDC 708852 (**3a**), CCDC 708853 (**5**), and CCDC 708851 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[15] ^{1}H NMR (300 MHz, [D$_8$]THF/CD$_2$Cl$_2$ = 3:2): $\delta = 7.34$ (s, 2H), 7.65 (s, 2H), 8.06 (s, 2H), 8.16 ppm (s, 2H), alkyl signals are hidden by product signals.