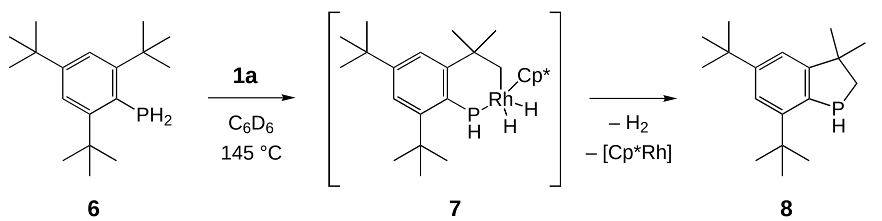

Scheme 2. Proposed mechanism for the formation of the cyclic phosphane **8** via rhodium(v) complex **7**.

phosphanes. In particular, the catalytic dehydrocoupling of secondary phosphanes is efficient and has been reported for the first time. Aryl and alkyl substituents are tolerated but reactivity is limited to sterically less demanding substrates. The resting state of the catalyst in the coupling of $HPPh_2$ is the diphosphanerhodium(I) complex **4** that is dominant throughout catalysis. Presumably, the reaction proceeds via a rhodium(v) species such as **5**. This catalytic reaction is advantageous over currently available methods for the synthesis of diphosphanes which produce stoichiometric amounts of salts as by-products.[17]

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The First Dectection of Peroxo and Bis-superoxo Complexes of Aluminum: $FAlO_2$ and $FAlO_4$**

Jan Bahlo, Hans-Jörg Himmel, and
Hansgeorg Schnöckel*

Peroxo and superoxo complexes are of major importance because of the role they play as oxygen carrier systems in biology[1] and in preparative chemistry.[2–4] For instance, peroxo complexes of vanadium show insulinomimetic properties[2] and complexes of rhenium are applied in olefin epoxidation.[3, 4] Another example from this class of compounds is hemocyanin, which contains a dinuclear copper site capable of binding O_2 in a μ-η^2:η^2 peroxo complex.[1] Finally, peroxo complexes are potential intermediates or products during the oxidation of metals or metal clusters.[5] Consequently, there is substantial interest in the exploration and isolation of new stable peroxo and superoxo complexes. Herein we report on the photolytically induced reaction of AlF with O_2 in solid argon matrices, which leads to the first known peroxo complexes and bis-superoxo complexes of aluminum, namely $FAlO_2$ and $FAlO_4$.[6] All products were identified and characterized on the basis of their IR absorptions (including the effects of isotopic changes ($^{16}O_2$, $^{18}O_2$, $^{16}O_2/^{18}O_2$, $^{16}O^{18}O$) and of quantum-mechanical calculations (ab initio (UHF and, in some cases, MP2) and density functional theory (DFT) calculations). In addition to their relevance for possible applications,[7] the title compounds show interesting electronic properties. While $FAlO_2$ exists in a singlet electronic ground state,[8] the $FAlO_4$ species exhibits a triplet ground state. The complexation of a second dioxygen molecule to $FAlO_4$ thus represents a spin-allowed process, and dioxygen complexes of this kind might well be of significant relevance as intermediates in oxidation processes.

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[*] Prof. Dr. H. Schnöckel, Dipl.-Chem. J. Bahlo, Dr. Dr. H.-J. Himmel
Institut für Anorganische Chemie
Universität Karlsruhe (TH)
Engesserstrasse, Geb. 30.45, 76133 Karlsruhe (Germany)
Fax: (+49) 721-608-4854
E-mail: hg@achpc9.chemie.uni-karlsruhe.de

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The reactions of AlF and $(AlF)_2$ with *one* O_2 molecule result in the formation of the peroxo species $FAlO_2$ and $FAl(\mu\text{-}O)_2AlF$, respectively.[9, 10] The presence of a third distinct species in the spectra for experiments with high dioxygen concentrations in the matrix shows that AlF is capable of binding a *second* O_2 moiety to give a molecule with the composition $FAlO_4$. $FAlO_2$ is the dominating species formed in the matrices for *low* O_2 concentrations (1 %), while $FAlO_4$ dominates for *high* O_2 concentrations (5–15 %).

Figure 1a shows an IR spectrum recorded upon UV photolysis ($\lambda_{max} = 254$ nm) of matrices containing AlF and 5 % $^{16}O_2$. Experiments with different oxygen isotopomers and different O_2 concentrations show that the spectrum contains signals attributed to three different reaction products. The first group of signals at 1077.3 and 781.8 cm^{-1} was assigned to product **1**, and the second group at 942.8 and 812.9 cm^{-1} to product **2**. The signals at 892.4 and 705.3 cm^{-1} were attributed to species **3**. For low O_2 concentrations (1 %), species **1** and **2** dominated, but species **3** gained intensity relative to **1** and **2** for higher O_2 concentrations (5 %). This might imply that **1** and **2** are products of the reaction with one O_2 unit, while **3** is the product of the reaction with two O_2 molecules.

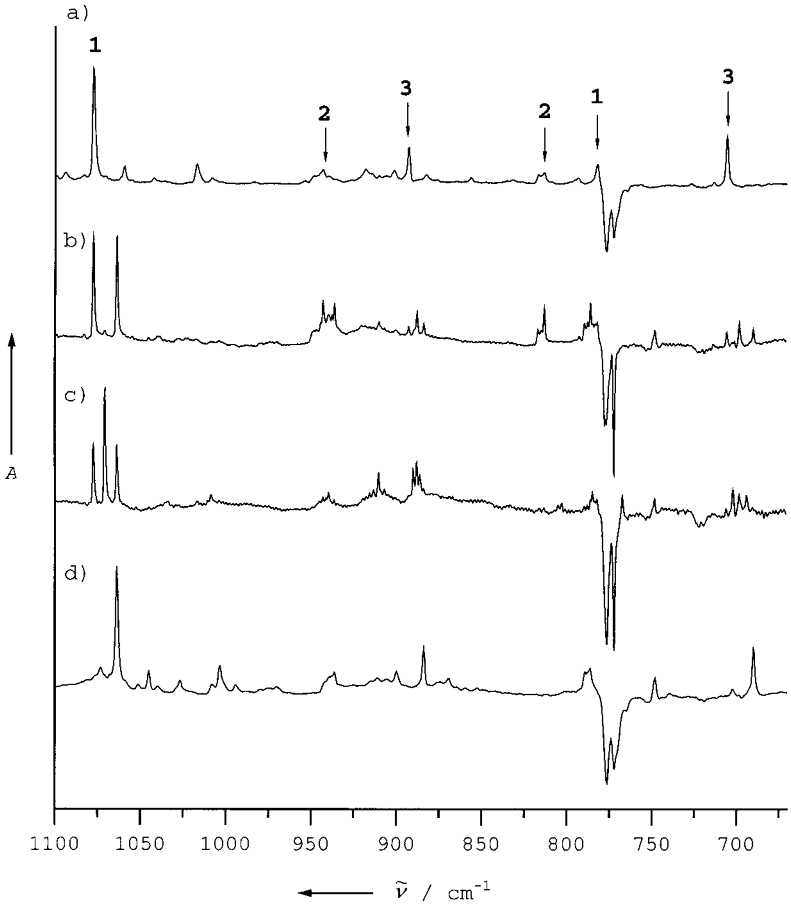
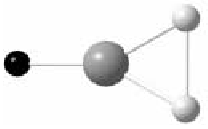


Figure 1. IR spectrum recorded after cocondensation of molecular AlF together with O_2 in a solid argon matrix followed by photolysis of the matrix with UV light ($\lambda_{max} = 254$ nm): a) $^{16}O_2$, b) $^{16}O_2/^{18}O_2$ (1:1 mixture), c) $^{16}O_2/^{16}O^{18}O/^{18}O_2$ (1:2:1 mixture), d) $^{18}O_2$.

Upon $^{16}O/^{18}O$ substitution, the signals due to product **1** were shifted to 1063.6 and 747.9 cm^{-1}, corresponding to $^{16}O/^{18}O$ ratios of 1.0132 and 1.0455, respectively (Figure 1 d). The signals due to species **2** exhibited red shifts of 6.6 and 27.3 cm^{-1} ($^{16}O/^{18}O = 1.0065$ and 1.0348, respectively). The absorptions due to product **3** were shifted to 883.7 and 689.9 cm^{-1}, implying $^{16}O/^{18}O$ ratios of 1.0102 and 1.0232, respectively. Other experiments with 1:1 mixtures of $^{16}O_2$ and $^{18}O_2$ revealed that the signals for **1** were found to be the superposition of the signals observed in the experiments using $^{16}O_2$ and $^{18}O_2$ separately (Figure 1 b). Two doublet features at 942.8/936.2 and 812.9/785.6 cm^{-1} in experiments with 1:1 mixtures of $^{16}O_2$ and $^{18}O_2$ could be assigned to **2**. Thus, it follows that **1** and **2** contain one O_2 group. By contrast, species **3** gave rise to extra signals that could not be accounted for merely by the superposition of the signals observed in the experiments using $^{16}O_2$ and $^{18}O_2$ separately. Following UV-photolysis two groups of absorptions associated with product **3** were observed to grow in, with three signals in each group. The signals of the first group were located at 892.4/887.6/883.7 cm^{-1}, that of the second group at 705.3/697.9/689.8 cm^{-1}. From this pattern it follows that **3** hosts two O_2 groups. Finally, the experiment was repeated by using 1:2:1 mixtures of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$. The two vibrational modes of **1** were now both split into triplets positioned at 1077/1070/1063 and 781/767/747 cm^{-1} (Figure 1 c). The bands due to **2** also showed triplet patterns, with the signals due to the $^{16}O^{18}O$ form of species **2** appearing at 939.4 and 802.7 cm^{-1}. Species **3** again gave rise to two groups of signals, but this time with as many as five signals in each group (892.4/889.7/887.6/885.9/883.7 and 705.6/701.5/697.9/693.5/689.8 cm^{-1}). This pattern indicates the presence of two pairs of equivalent O atoms.

Herein we will focus the discussion mainly on species **1** and **3**; species **2** will be discussed in detail elsewhere.[9] The results of the experiments indicate that these species have the composition $FAlO_2$ (**1**) and $FAlO_4$ (**3**), which would be better discribed as $FAl(O_2)_2$. Our DFT calculations resulted in the global minimum structures shown for **1** and **3**.



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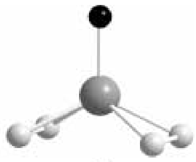

3

Species **1** and **3** both exhibit C_{2v} symmetry with Al–F distances of 1.6340 and 1.6552 Å, respectively, which are typical values for Al–F bonds found in three-coordinate Al^{III} species (e.g. AlF_3 1.631(3) Å[11]). The O–O bond length in **1** is 1.6637 Å, whereas that in **3** (1.3673 Å) is, as expected, significantly shorter, but in good agreement to the distance expected for O_2^- (1.3519 Å according to DFT calculations with the B3LYP basis set). The O-Al-O angle is 58.4° in **1** and

Table 1. Observed and calculated spectra of $FAl(^{16}O_2)$, $FAl(^{18}O_2)$, and $FAl(^{16}O^{18}O)$ (**1**).[a]

	$FAl(^{16}O_2)$			$FAl(^{18}O_2)$			$FAl(^{16}O^{18}O)$		
obs.	calcd[b]		obs.	calcd[b]		obs.	calcd		Assignment
	MP2/TZVPP	B3LYP/6-311G*		MP2/TZVPP	B3LYP/6-311G*		MP2/TZVPP	B3LYP/6-311G*	
1077.3	1087.7 (147)	1114.4 (144)	1063.6	1074.4 (149)	1098.9 (146)	1070.7	1081.2 (148)	1106.8 (145)	ν_1 (a_1)
–[d]	720.4 (13)	739.8 (14)	–[d]	696.6 (9)	715.7 (9)	–[d]	706.6 (12)	724.0 (12)	ν_2 (a_1)
–[d]	525.6 (12)	528.2 (12)	–[d]	501.6 (12)	504.5 (12)	–[d]	513.9 (12)	516.6 (12)	ν_3 (a_1)
–[c]	238.2 (119)	238.5 (121)	–[c]	236.2 (116)	236.6 (118)	–[c]	237.2 (117)	237.6 (120)	ν_4 (b_1)
781.8	810.6 (66)	782.4 (19)	747.9	775.8 (66)	748.1 (20)	766.8	794.8 (65)	768.8 (19)	ν_5 (b_2)
–[c]	224.5 (74)	217.7 (73)	–[c]	220.6 (70)	213.9 (69)	–[c]	222.5 (72)	215.8 (71)	ν_6 (b_2)

[a] Frequencies in cm^{-1}, intensities in $km\,mol^{-1}$ in parentheses. [b] C_{2v} symmetry; geometry (bond lengths in Å, angles in °): MP2/TZVPP: Al–F 1.6430, Al–O 1.7006, O–O 1.6596, O-Al-O 58.4; B3LYP/6-311G*: Al–F 1.6390, Al–O 1.7102, O–O 1.6637, O-Al-O 58.4. [c] Out of range of detection. [d] Too weak to be detected.

Table 2. Observed and calculated spectra of $FAl(^{16}O_2)_2$, $FAl(^{18}O_2)_2$, and $FAl(^{16}O^{18}O)_2$ (**3**).[a]

$FAl^{16}O_4$		$FAl^{18}O_4$		$FAl^{16}O_2{}^{18}O_2$		
obs.	calcd[b]	obs.	calcd[b]	obs.	calcd	Assignment
–[d]	1138.6 (2)	–[d]	1074.0 (3)	–[d]	1136.8 (5)	ν_1 (a_1)
892.4	900.6 (151)	883.7	898.9 (149)	887.6	899.8	ν_2 (a_1)
–[d]	506.9 (9)	–[d]	486.0 (10)	–[d]	496.2 (10)	ν_3 (a_1)
–[c]	186.1 (20)	–[c]	178.9 (18)	–[c]	182.5 (19)	ν_4 (a_1)
–[d]	404.7 (0)	–[d]	380.6 (0)	–[d]	390.8 (0)	ν_5 (a_2)
–[c]	69.9 (0)	–[c]	65.9 (0)	–[c]	67.8 (0)	ν_6 (a_2)
–[d]	490.6 (1)	–[d]	467.2 (2)	–[d]	479.9 (1)	ν_7 (b_1)
–[d]	242.5 (50)	–[d]	238.3 (38)	–[d]	240.2 (49)	ν_8 (b_1)
–[c]	176.0 (0.01)	–[c]	166.9 (0.03)	–[c]	171.4 (0.03)	ν_9 (b_1)
–[d]	1135.1 (12)	–[d]	1071.0 (9)	–[d]	1072.5 (6)	ν_{10} (b_2)
705.3	714.3 (179)	689.9	694.2 (175)	697.9	701.5 (177)	ν_{11} (b_2)
–[d]	205.3 (26)	–[d]	199.6 (24)	–[d]	201.8 (24)	ν_{12} (b_2)

[a] Frequencies in cm^{-1}, intensities in $km\,mol^{-1}$ in parentheses. [b] C_{2h} symmetry; geometry (bond lengths in Å, angles in °): B3LYP/6–311G*: Al–F 1.6552, Al–O 1.8562, O–O 1.3673, O-Al-O 43.2. [c] Out of range of detection. [d] Too weak to be detected or IR silent.

43.2° in **3** (for O atoms of the same O_2 unit), and as a consequence, the Al–O distance increases from 1.7006 Å in **1** to 1.8562 Å in **3**.[12]

The calculated vibration frequencies for **1** and **3** are compared with the experimental values in Table 1 and Table 2, respectively.[13] The calculations predict in both cases two of the six or twelve, respectively, modes to carry sufficient intensity to guarantee their detection subject to the molecule being formed in sufficient yields. This is in agreement to the experiments which provide in both cases clear evidence for two strong absorptions. The observed frequencies of these two modes are in good agreement with the calculated values.

The ab initio calculations for **1** at the MP2 level of theory and using a TZVPP type basis set resulted, in agreement with the DFT calculations, in a global minimum structure with C_{2v} symmetry (singlet electronic ground state). The Al–O and O–O distances of 1.7006 and 1.6596 Å, respectively, are somewhat shorter than those predicted on the basis of the DFT calculations. The Al–F bond length and the O-Al-O angle are 1.6430 Å and 58.4°, respectively. The following frequencies (in cm^{-1}) were calculated for $FAl^{16}O_2$ (symmetry assignment and intensity [$km\,mol^{-1}$] in parentheses): 1087.7 (a_1, 147), 810.6 (b_2, 66), 720.4 (a_1, 13), 525.6 (a_1, 12), 238.2 (b_1, 119), 224.5 (b_2, 74).

Ab initio calculations for **3** at the HF level of theory with a 6-311G*-type basis set also gave a triplet electronic ground state, which is now slightly distorted from C_{2v} symmetry, resulting in only C_2 symmetry. Thus two different values are obtained for the Al–O distances of one O_2 (1.8798 and 1.7849 Å). Other geometrical parameters (bond lengths in Å, angles in °) are: Al–F 1.6327, O–O 1.3030, F-Al-O 112.7/120.4, O-Al-O 40.6 (for O atoms of one O_2 unit). As expected, the frequency calculation using the HF method resulted in wavenumbers higher than those calculated using DFT methods. The following frequencies (in cm^{-1}) were calculated for $FAl(^{16}O_2)_2$ (symmetry assignment and intensity [$km\,mol^{-1}$] in parentheses): 1329.3 (b, 101), 1320.0 (a, 9), 954.1 (a, 185), 797.1 (b, 273), 569.8 (a, 6), 388.2 (b, 51), 300.9 (a, 7), 220.0 (b, 33), 211.8 (b, 22), 199.8 (a, 24), 175.2 (b, 2), 124.2 (a, 0.09). Attempts to calculate the structure and frequencies for **3** using the MP2 method were less successful. The MP2 method appears to be generally less reliable for the computation of O_2-containing molecules such as **3**.

Mode coupling makes an assignment of the absorptions almost impossible. Therefore a normal coordinate analysis was carried out for all molecules. Force constants of 247 and 585 $N\,m^{-1}$ were derived for the O–O stretching force constant *f*(O–O) of **1** and **3**, respectively, and values of 660 and 190 $N\,m^{-1}$ were calculated for O_2^- and O_2^{2-}, respectively. The stretching force constants *f*(Al–F) and *f*(Al–O) of the Al–F and Al–O bonds are 597 and 445 $N\,m^{-1}$, respectively, for **1** and 493 $N\,m^{-1}$ and 193 $N\,m^{-1}$, respectively, for **3**.[14] A detailed analysis of the bonding properties within triplet **3** proved difficult, and so far we were not able to establish a clear picture of the frontier orbitals and the charge distribution. However, the O–O distance and force constant support the presence of O_2^- units coordinated to the aluminum center. This would imply that the unpaired electrons are located at the O_2^- groups with only weak coupling between the two groups.

In the same way,[9] experiments with AlCl and AlBr in place of AlF provided evidence for the generation of $ClAlO_2$, $ClAl(O_2)_2$, $BrAlO_2$, and $BrAl(O_2)_2$ as products of the photolytically induced matrix reaction of AlCl with *one* or *two* O_2 molecules. This observation supports the presented assignment of **1** and **3**.

The characterization of the peroxo and bis-superoxo complexes **1** and **3** provides the opportunity to compare these complexes with previously investigated systems with similar structure: In the peroxovanadium imidazole monoanion O–O distances are 1.475(2) and 1.467(3) Å, which are thus similar to the value for the O–O distance in $FAl(O_2)_2$. An example for a peroxorhenium complex is $[CH_3Re(O_2)_2O]$, which has been studied in the gas phase by using electron diffraction[3] and exhibits O–O and Re–O distances of 1.451(6) and 1.67(1) Å, respectively. $[(Ph_3P)_2PtO_2]$ exhibits a O–O bond length of 1.26 Å,[18] which is shorter than the value of 1.3520 Å calculated for O_2^-. In $[\{Cu[HB(3,5\text{-}i\text{Pr}_2pz)_3]\}_2(O_2)]$, which might serve as a model compound for oxohemocyanin,[19] the O–O distance is 1.41 Å and is thus significantly longer than the calculated value for O_2^- (1.3520 Å), but shorter than that for O_2^{2-} (1.6258 Å).

Superoxo and peroxo complexes of main group elements are very rare. The Group 1 elements form ionic MO_2 complexes with C_{2v} symmetry.[20] Of the Group 2 element compounds MgO_2 is known.[21–24] Oxygen compounds of Group 13 have also been frequently studied.[25–29] $FAlO_2$ is also structurally similar to $OSiO_2$ and F_2SiO_2, which have both been charaterized by IR spectroscopy in matrix isolation experiments.[30–32] One of the few examples of a main group element bis-superoxo complex is $Mg(O_2)_2$.[21–24] It is noteworthy that alkali metals are capable of binding not only one but also two dioxygen molecules.[20] All these compounds will be discussed and compared with $XAlO_2$ and $XAl(O_2)_2$ (X = F, Cl, or Br) in detail elsewhere.[9]

In Figure 2 the energies for **1** and **2** are compared relative to molecular AlF and two oxygen molecules. We note that the reaction of AlF with the first O_2 molecule is less exothermic ($\Delta E = -140.5\ \mathrm{kJ\,mol^{-1}}$) than the reaction of $FAlO_2$ with the second oxygen molecule to give $FAl(O_2)_2$ ($\Delta E = -152.3\ \mathrm{kJ\,mol^{-1}}$).

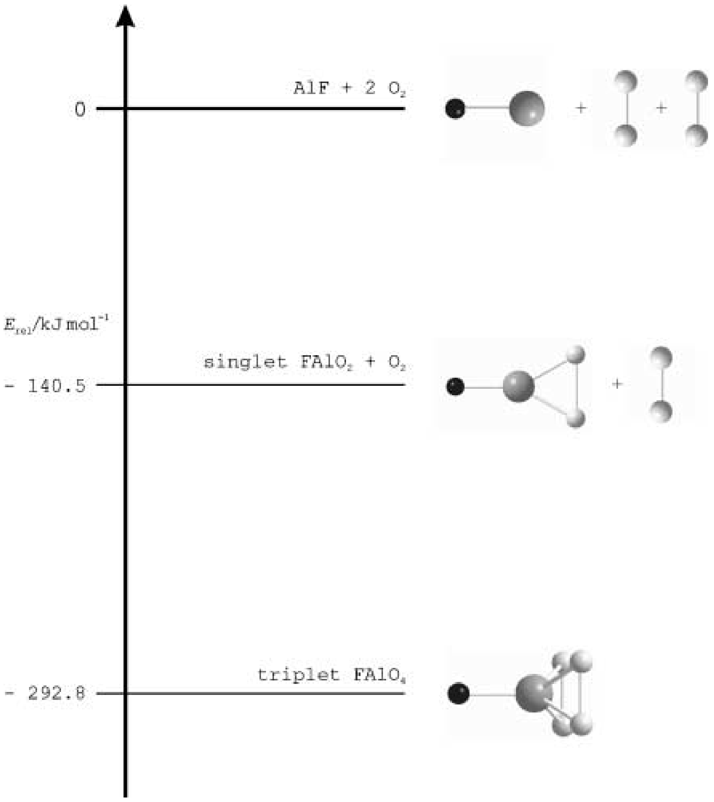

Figure 2. Energies of **1** and **2** relative to the energies of the starting materials AlF and O_2.

We propose that **1** and **3** occur as intermediates in the oxidation of AlF to give solid FAlO. Although the structure of FAlO is unknown, it is expected to show similarities to the structure of isoelectronic SiO_2. This conclusion seems plausible since the reaction (1) has been calculated to be

(1)

exothermic ($-81.8\ \mathrm{kJ\,mol^{-1}}$) and the molecule $FAl(\mu\text{-}O_2)AlF$,[9] like the dimer of SiO_2 ($OSi(\mu\text{-}O_2)SiO$),[33] could be the next intermediate to the solid-state materials FAlO and SiO_2, respectively. Possibly species like **3**, in which two O_2 units are coordinated to the metal atom, may also play a major role as intermediates in many oxidation processes, for example of metal atom clusters or metal surfaces.

Experimental Section

Details of the setup of our matrix apparatus can be found in reference [34]. The subhalogenide AlF was generated in a Knudsen-type graphite cell by passing CHF_3 (Messer, 99.995 %) over Al (Merck, 99.999 %), heated resistively to 900 °C. The AlF molecules produced in this process were deposited together with an excess of O_2-doped argon onto a copper block kept at 13 K by means of a closed-cycle cryostat (Leybold LB 510). Immediately after deposition the matrices were investigated by IR spectroscopy. Subsequently the matrices were photolyzed with UV radiation and the photolytically induced reactions again monitored by IR spectroscopy.

The IR spectra were recorded on a Bruker 113v spectrometer, equipped with an MCT and a DTGS detector. The spectra were recorded with a resolution of 0.5 cm^{-1} (MCT detector) and 1.0 cm^{-1} (DTGS detector).

UV-photolysis ($\lambda_{max} = 254$ nm) was performed with a low-pressure Hg lamp (Gräntzel, Karlsruhe) operating at 200 W.

The chemicals used for the matrix reactions were purchased from the following sources and with the quoted purities: $^{16}O_2$: Messer, 99.9998 %, $^{18}O_2$: Prochem, 99.1 %, Ar: Messer, 99.9998 %.

Ab initio UHF and density functional theory (B3LYP) calculations were carried out with the Gaussian 98 program package[35] and a 6-311G(d)-type basis set was used. Ab initio (MP2) calculations were carried out with the RIMP2 module[36] of the TURBOMOLE program package[37] with a TZVPP-type basis set.

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[12] The larger Al–O distance in **3** is in agreement with the values found in other highly coordinated Al compounds. For example, the Al–O bond lengths in the octahedral $[Al(O_2)(acac)_3]$ (acac = acetyl acetonate) complex is 1.89 Å (N. Ya. Turova, V. A. Kozunov, A. I. Yanovskii, N. G. Bokii, Yu. T. Struschkov, B. L. Tarnopolskii, *J. Inorg. Nucl. Chem.* **1979**, *41*, 5).

[13] The calculations give the following frequencies [in cm^{-1}] for the other isotopomers of **3** (with intensity [in $km\,mol^{-1}$] and symmetry assignment in parentheses): 1074.0 (3, a_1), 898.9 (149, a_1), 486.0 (10, a_1), 178.9 (18, a_1), 380.6 (0, a_2), 65.9 (0, a_2), 467.2 (2, b_1), 238.3 (38, b_1), 166.9 (0.03, b_1), 1071.0 (9, b_2), 694.2 (175, b_2), 199.6 (24, b_2) for $FAl(^{18}O_2)_2$, and 1136.8 (5, a_1), 899.8 (150, a_1), 496.2 (10, a_1), 182.5 (19, a_1), 390.8 (0, a_2), 67.8 (0, a_2), 479.9 (1, b_1), 240.2 (49, b_1), 171.4 (0.03, b_1), 1072.5 (6, b_2), 701.5 (177, b_2), 201.8 (24, b_2) for $FAl(^{16}O)_2(^{18}O)_2$.

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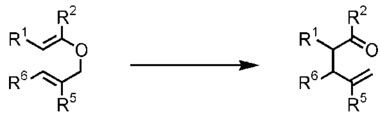
The Catalytic Enantioselective Claisen Rearrangement of an Allyl Vinyl Ether**

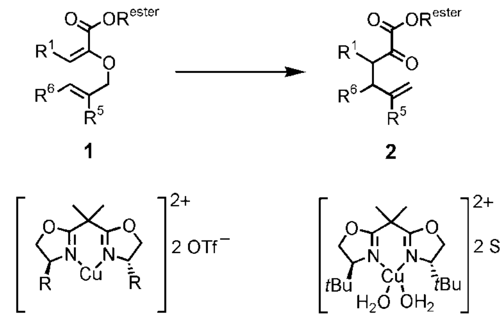
Lars Abraham, Regina Czerwonka, and
Martin Hiersemann*

The [3,3]-sigmatropic rearrangement of an allyl vinyl ether was described by Claisen for the first time in 1912.[1] Since then this rearrangement, which was named after him, has been developed into one of the most powerful C–C bond forming methods (Scheme 1).[2] There are various approaches to carry out the Claisen rearrangement and related [3,3]-sigmatropic rearrangements enantioselectively by using chiral reagents.[3, 4] The only catalytic enantioselective [3,3]-sigmatropic rearrangement known to date was described for allyl imidates.[5] Yamamoto et al. used chiral Lewis acids based on Al^{III} for the enantioselective Claisen rearrangement of acyclic, aliphatic allyl vinyl ethers. However, 1–2 equivalents of the chiral Lewis acid are required and the range of substrates is very select.[6]



Scheme 1. The Claisen rearrangement of an allyl vinyl ether. Which catalysts are able to catalyze this process diastereo- and enantioselectively?

In our search for a chiral catalyst for the Claisen rearrangement of 2-alkoxycarbonyl-substituted allyl vinyl ethers **1**, we found the combination of $Cu(OTf)_2$ and a molecular sieve to be suitable.[7] In an extension of this work, we now report the use of chiral copper(II) bis(oxazoline) ($[Cu^{II}(box)]$) complexes as catalysts for the Claisen rearrangement (Scheme 2).



3 (R = Ph): $[Cu\{(S,S)\text{-Ph-box}\}](OTf)_2$ **5**: $[Cu\{(S,S)\text{-}t\text{Bu-box}\}](H_2O)_2(SbF_6)_2$
4 (R = *t*Bu): $[Cu\{(S,S)\text{-}t\text{Bu-box}\}](OTf)_2$

Scheme 2. General substrate structure and the catalysts used.

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[*] Dr. M. Hiersemann, L. Abraham, R. Czerwonka
Institut für Organische Chemie
Technische Universität Dresden
01062 Dresden (Germany)
Fax: (+49) 351-463-33162
E-mail: martin.hiersemann@chemie.tu-dresden.de

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