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Figure 1. Crystal structure of  $Ba_2Nd_7Si_{11}N_{23}$ , viewed along [001]. Left: the  $SiN_4$  tetrahedra are shown as closed polyhedra,  $Ba^{2+}$  as gray spheres, and  $Nd^{3+}$  as white spheres. Right: topology of the Si-N network; only the Si tetrahedral centers are directly connected.



Figure 2. Sectional view of the wide  $Si_8N_8$  ring channels ([001] **8** 285 × 438 pm<sup>2</sup>) in  $Ba_2Nd_7Si_{11}N_{23}$ . Left: coordination of the  $Ba^{2+}$  ions (coordination number 16). Right: the free diameter of the channels is calculated from the atomic coordinates considering the ionic radius of  $N^{3-}$  (146 pm); cf. also ref. [6].

bound to the nitrogen atoms of the Si-N network structures. The  $Ba^{2+}$  ions in the open channels of  $Ba_2Nd_7Si_{11}N_{23}$  seem to be predestined for this procedure.

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- [9] In a typical batch 0.4 mmol Ba, 1.3 mmol Nd, and 2 mmol Si(NH)<sub>2</sub> were thoroughly mixed under inert gas atmosphere in a glove box and transferred in a tungsten crucible into the high-frequency furnace. Under nitrogen atmosphere the reaction mixture was heated to 900°C in 7 h and over a further 18 h to 1650°C followed by a cooling over 15 h to 1400°C and in another 15 min to room temperature.

- [10] The X-ray amorphous product obtained by ammonolysis of SiCl<sub>4</sub> has the approximate composition Si(NH)<sub>2</sub>. Despite its undefined character, silicon diimide is an important precursor for the technical production of Si<sub>3</sub>N<sub>4</sub>. Cf. H. Lange, G. Wötting, G. Winter, Angew. Chem. 1991, 103, 1606; Angew. Chem. Int. Ed. Engl. 1991, 30, 1579.
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- [12] Ba<sub>2</sub>Nd<sub>7</sub>Si<sub>11</sub>N<sub>33</sub>: Cmmm, a = 1096.20(6), b = 2304.60(14), c = 964.85(5) pm, Z = 4, Siemens P4 diffractometer, Mo<sub>Ka</sub> radiation, graphite monochromator, F(000) = 3388.0,  $\mu(Mo_{Ka}) = 18.39 \text{ mm}^{-1}$ ,  $\omega \text{ scan}$ , 14287 measured reflections in the range  $2^{\circ} \leq 2\theta \leq 60^{\circ}$ , 2021 unique reflections with  $F_o^2 \geq 20 \langle F_o^2 \rangle$ , empirical absorption correction ( $\psi$  scans),  $R_{\text{int}} = 0.0472$ ; the crystal structure was solved by direct methods (SHELXTL, Vers 5.03) and anisotropically refined by a least-squares procedure against  $F^2$  with all data, 32 refined parameters, RI =

0.0440, wR2 = 0.0884, GOF = 0.973. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karls-ruhe, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-407202.

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- [14] Network structures of connected SiN₄ can be characterized topologically by the cycle -class sequence. It specifies the relative abundance of Si<sub>2</sub>N<sub>4</sub> ring sizes (for n = 1, 2, 3...) per unit cell. Cycle class sequence of Ba<sub>2</sub>Nd<sub>7</sub>Si<sub>11</sub>N<sub>23</sub>: {-,0,6,1,0,12,24,30...}. Cf. also: a) W. E. Klee, Z. Kristallogr. 1987, 179, 67; b) A. Beukemann, W. E. Klee, *ibid.* 1994, 209, 709.
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### Alkylrhenium Oxides from Perrhenates: A New, Economical Access to Organometallic Oxide Catalysts\*\*

Wolfgang A. Herrmann,\* Roland M. Kratzer, and Richard W. Fischer

Organometallic oxides have been thoroughly investigated, particularly because some representatives of this ever-growing class of compounds exhibit a variety of catalytic properties.<sup>[1]</sup> One of the main reasons behind our interest in rhenium is the diverse catalytic successes of methyltrioxorhenium (MTO).<sup>[2]</sup> This has recently been reported to catalyze different oxidation processes.<sup>[2-4]</sup> Twenty years after MTO was first observed,<sup>[5]</sup> two synthetic pathways have become established for access to organorhenium(VII) oxides:

<sup>[\*]</sup> Prof. Dr. W. A. Herrmann, R. M. Kratzer Anorganisch-chemisches Institut der Technischen Universität München Lichtenbergstrasse 4, D-85747 Garching (Germany) Fax: Int. code + (89)289-13473 e-mail: herrmann@zaphod.anorg.chemie.tu-muenchen.de
Dr. R. W. Fischer Corporate Research & Technology, Hoechst AG, Frankfurt am Main

<sup>(</sup>Germany)

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1) Direct alkylation of dirhenium heptoxide ( $Re_2O_7$ ) with tetraalkyltin or dialkylzinc. However, in this case 50% of the rhenium is lost in the form of unreactive trialkylstannyl- and zinc perrhenate.<sup>[6]</sup> 2) Alkylation of  $Re_2O_7$  in the presence of trifluoroacetic anhydride. Here, the formation of rheniumcontaining by-products is suppressed, but the anhydride used is expensive and rather sensitive.<sup>[7]</sup>

The disadvantage of both these methods is that the  $Re_2O_7$ starting material is extremely moisture sensitive. Now for the first time, a simple one-pot reaction facilitates the use of a wide variety of easily accessible perrhenates as starting compounds. MTO 1, for example, can be synthesized in excellent yields without the rigorous exclusion of air and moisture (Table 1). The perrhenates  $(M[ReO_4]_n, n=1, 2 \text{ and})$ 



Table 1. Direct synthesis of organorhenium(VII) oxides from perrhenates (solvent: acetonitrile).

	Perrhenate	Alkylation reagent	Condi t (h)	itions T (°C)	Yield RReO <sub>3</sub> (%)[a]
1	Ag[ReO <sub>4</sub> ]	(CH <sub>3</sub> ) <sub>4</sub> Sn	12	25	76
2	$Ca[ReO_4]_2$	(CH <sub>3</sub> ) <sub>4</sub> Sn	4	81	78
3	$Na[ReO_4]$	(CH <sub>3</sub> ) <sub>4</sub> Sn	4	81	70
4	K[ReO <sub>4</sub> ]	(CH <sub>3</sub> ) <sub>4</sub> Sn	24	25	63
5	$NH_4[ReO_4]$	(CH <sub>3</sub> ) <sub>4</sub> Sn	24	25	56
6	$Zn[ReO_4]_2$	(CH <sub>3</sub> ) <sub>4</sub> Sn	12	25	86[b]
7	(CH <sub>3</sub> ) <sub>3</sub> SnReO <sub>4</sub>	(CH <sub>3</sub> ) <sub>4</sub> Sn	24	25	77 b
8	Na[ReO <sub>4</sub> ]	Bu <sub>3</sub> SnCH <sub>3</sub>	4	81	46
9	$Ag[ReO_4]$	$Zn(C_2H_5)_2$	12	0	36
10	$Na[ReO_4]$	$Zn[(CH_3)_2NC_3H_6]_2$	12	0	25

[a] Isolated yield except the marked examples 6 and 7. [b] GC yield  $(\pm 5\%)$ .

 $M = Ag^+$ ,  $K^+$ ,  $Na^+$ ,  $Zn^{2+}$ ,  $Ca^{2+}$ ,  $NH_4^+$ ; (CH<sub>3</sub>)<sub>3</sub>SnReO<sub>4</sub>) are then treated with chlorotrimethylsilane and tetramethyltin. The addition of one equivalent of H<sub>2</sub>SO<sub>4</sub> is recommended if only scarcely soluble perrhenates are used. With alkylzinc compounds this new synthetic route can be extended to the preparation of homologues of 1 and to alkyl-functionalized derivatives. For instance, ethyltrioxorhenium(VII) (2) is produced in 36% yield.<sup>[8]</sup> In addition, the oxidation catalyst [3-(dimethylamino)propyl]trioxorhenium(VII) (3) could be prepared by using this new method.<sup>[9]</sup>

A key advantage of this new route is the possibility of catalyst recycling in MTO-catalyzed oxidation processes; the perrhenates can be separated from exhausted catalyst solutions through simple precipitation of the perrhenic acid from the solution. This new aspect sets the industrial application of rhenium catalysts in a realistic context.

The synthesis proceeds as exemplified for MTO 1 (Scheme 1): First perrhenate is converted to trimethylsilyl perrhenate (4) and the respective metal chloride (1).<sup>[10,11]</sup> The next step is a condensation of two activated perrhenates 4(2). The resulting dirhenium heptoxide is then cleaved with (the second equivalent of) chlorotrimethylsilane to give chlorotrioxorhenium (5) and 4(3); the final alkylation of 5(4)affords MTO 1.

This new synthetic strategy represents an economical and simple access to organorhenium oxides from a plethora of readily available, rather cheap perrhenates. An extension of



Scheme 1. Synthetic steps in the formation of methyltrioxorhenium from perrhenates.

this concept to the neighboring elements of the periodic table seems feasible. One of our future goals is the activation of simple oxo salts (Cr, Mo, W, Mn) with chlorotrimethylsilane<sup>[11]</sup> with the aim of synthesizing novel organometallic oxides.

#### **Experimental Section**

The perrhenates were prepared by oxidation of rhenium with  $H_2O_2$  (30%) and precipitation (KCl, AgNO<sub>3</sub>) or neutralization (e.g., NaOH, Ca(OH)<sub>2</sub>). Zn[ReO<sub>4</sub>]<sub>2</sub> and (CH<sub>3</sub>)<sub>3</sub>SnReO<sub>4</sub> were formed as by-products in the synthesis of organorhenium oxides [6,8]. Unless mentioned otherwise, acetonitrile (Merck, p. A.) was used without further purification or drying procedures. Chlorotrimethylsilane (98%, Aldrich) was distilled prior to use

CH3ReO31: Attention! Tetramethyltin and trimethyltin chloride are very toxic and volatile. All transformations are therefore to be performed in a hood. Ag[ReO<sub>4</sub>] (1.00 g, 2.79 mmol) was dissolved in CH<sub>3</sub>CN (20 mL) in a sealable 50-mL Erlenmeyer flask. After the addition of ClSi(CH<sub>3</sub>)<sub>3</sub> (0.78 mL, 6.14 mol), a white precipitate was formed immediately. To the suspension Sn(CH<sub>3</sub>)<sub>4</sub> (0.43 mL, 3.07 mol) was added and the mixture was stirred for 12 h at 25 °C. It was then filtered and the resulting yellow solution was evaporated in a Schlenk tube under reduced pressure (20 mbar). Due to the volatility of the tin compounds it is recommended that a trap cooled with nitrogen is installed between the Schlenk tube and the pump. The residue was sublimed at ambient temperature under high vacuum (10<sup>-2</sup> mbar). Compound 1 was obtained in 76% yield (696 mg, m.p. 108°C).

Na[ReO<sub>4</sub>] (1.00 g, 3.66 mmol) was suspended in CH<sub>3</sub>CN (20 mL) in a 50-mL round-bottomed flask. After the addition of ClSi(CH<sub>3</sub>)<sub>3</sub> (1.02 mL, 8.05 mol) and Sn(CH<sub>3</sub>)<sub>4</sub> (0.56 mL, 4.03 mol) the reaction mixture was heated to reflux for 4 h. Then the cooled mixture was filtered and the yellow-orange solution was evaporated to dryness in a Schlenk tube under reduced pressure (20 mbar). The residue was sublimed at ambient temperature under high vacuum (10<sup>-2</sup> mbar). Compound 1 was obtained in 70% yield (639 mg, m.p. 108 °C).

K[ReO<sub>4</sub>] (8.70 g, 0.03 mol) was suspended in CH<sub>3</sub>CN (150 mL) in a 250-mL flask with a faucet. Concentrated H2SO4 (1.6 mL, 0.03 mol), ClSi(CH3)3 (8.30 mL, 0.066 mol), and  $Sn(CH_3)_4$  (4.2 mL, 0.03 mol) were added and the reaction mixture was stirred at 25 °C for 24 h. Then the solution was evaporated to dryness without filtration at 20 mbar and the black residue was extracted with n-pentane  $(4 \times 50 \text{ mL})$  for several hours each time. The combined extracts were evaporated to about 30 mL and maintained at - 35 °C for 24 h. The precipitating MTO still contained Me<sub>3</sub>SnCl and was therefore purified by sublimation (25°C, 10<sup>-2</sup> mbar). Yield: 63% (4.71 g). If the melting point of this MTO fraction is still below 100 °C, a second sublimation must follow.

(CH<sub>3</sub>)<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>ReO<sub>3</sub> 3: Na[ReO<sub>4</sub>] (0.50 g, 1.83 mmol) was suspended in dry CH<sub>3</sub>CN (10 mL) under the exclusion of air and treated at -40 °C with ClSi(CH<sub>3</sub>)<sub>3</sub> (0.46 mL, 3.66 mmol) and Zn[(CH<sub>3</sub>)<sub>2</sub>NC<sub>3</sub>H<sub>6</sub>]<sub>2</sub> (0.43 g, 1.83 mmol). The mixture was stirred at 0°C for 12 h. Then the solution was evaporated to dryness and the residue was extracted with *n*-pentane  $(3 \times 5 \text{ mL})$ . The combined extracts were evaporated and kept in a cool place. Compound 3 precipitated from the solution in 25% yield. Elemental analysis for C5H12NO3Re (320.4): calcd. C 18.69, H 3.77, N 4.36; found C 18.76, H 4.00, N 4.08; IR (KBr):  $\bar{\nu} = 960 \text{ cm}^{-1}$ (Re=O), 917 (Re=O); 'H NMR (200 MHz, CD<sub>3</sub>CN, 20°C):  $\delta = 2.20$  (s, 6H, NCH<sub>3</sub>), 2.85 (t, 2H, NCH<sub>2</sub>), 3.02 (m, 2H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 3.50 (t, 2H, ReCH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (200 MHz, CD<sub>3</sub>CN, 20 °C):  $\delta = 57.3$  (NCH<sub>3</sub>), 80.2 (NCH<sub>2</sub>), 47.2 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 28.4 (ReCH<sub>2</sub>)

CH3CH2ReO3 2: The preparation of 2 was performed with Zn(CH2CH3)2 under analogous conditions to those employed for 3. Yield: 36%.

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## **Repetitive Construction of Macrocyclic** Oligophenylenes\*\*

Volker Hensel, Karola Lützow, Joel Jacob, Katrin Gessler, Wolfram Saenger, and Arnulf-Dieter Schlüter\*

Cyclic oligophenylenes<sup>[1]</sup> and related compounds with conformationally rigid structures<sup>[2]</sup> have attracted the interest of chemists for issues including aromaticity, host-guest chemistry, aggregation behavior, and molecular constructions. Repetitive strategies are of importance in synthetic chemistry whenever structurally defined and monodispersive molecular objects in the nm range are targeted.<sup>[3]</sup> Recently Moore<sup>[4a]</sup> and Höger<sup>[4b]</sup> applied this concept to hexagonal macrocycles with phenylacetylene units. Stimulated by these studies and given the experience in our group with Suzuki cross-coupling reactions,<sup>[5]</sup> we decided to develop a repetitive synthesis of soluble, regular macrocyclic oligophenylenes.

Macrocycles  $1 \ (n=0, 1)$  were selected as initial targets because they are the smallest cyclic hexagonal oligophenylenes in which the unavoidable solubilizing groups can be attached at the sides and not the corners. This leaves the option of introducing substituents at the latter, for example, for the construction of further macrocycles. The synthesis of **1** was achieved by subjecting a variety of kinked oligophenylene telechelics (modules)<sup>[6]</sup> to Suzuki cross-coupling.<sup>[7]</sup> They may be classified as either AB-type modules consisting of six (**2**, **4**) and twelve phenylene units (**3**, **5**) or AA- and BB-type modules consisting of three (**6a**) [**6b**: five] and five phenylene units (**7a**) [**7b**: seven], respectively.<sup>[8]</sup> For each module the conditions such as solvent, kind of catalyst and its relative amount, dilution, kind of base, temperature, scale of reaction, and reaction time were systematically optimized in order to gain maximum insight into the factors which influence these ring-closing reactions.<sup>[9,10]</sup>

The optimized yields are given in Scheme 1. They allow a number of conclusion to be drawn: a) Each of the routes actually furnishes macrocycle 1,<sup>[11]</sup> however, the yields vary considerably (13-85%); b) neither module 2 nor 3 gives satisfactory yields; c) bromide is apparently far inferior to iodide; d) yields are highest (85%) if iodo telechelics are used that already carry the required number of phenylene units (5a,b); e) coupling of smaller telechelics (4a,b) saves three steps but leads to a decrease in yield (35-40%), regardless of whether the AA/BB- or AB-type approach is chosen;<sup>[12]</sup> f) pinacole esters of boronic acids are somewhat superior to the corresponding free acids with regard to coupling efficiency (for example, see the reaction of 5b versus that of 5a); handling and spectroscopic characterization of esters is also more convenient; g) the best results are generally obtained under high dilution using a syringe pump.<sup>[10]</sup> Conclusion b) deserves further comment: The Br/(BOR)<sub>2</sub> substitution pattern more or less fails with regard to ring formation because deboronification is no longer a wellknown side reation<sup>[5a,13]</sup> but a main reaction. For example, the attempted coupling of 3a gave, besides a few percent of desired ring 1b, the deboronified starting compound and a deboronified noncyclic dimer in yields of approximately 43% each (HPLC). Clearly, deboronifaction and linear growth overrides ring closure.[14]

To accumulate knowledge on conformational characteristics of these oligophenylenes, in particular with regard to the relative positioning of the corners, attempts were made to crystallize 1b.<sup>[15]</sup> Unfortunately these failed; flexible chains introduced to enhance solubility often reduce the ability of the compound to crystallize. However, crystals of 1a could be grown from a solution in chloroform/ethanol, and the crystal structure of 1a was solved by X-ray diffraction.[16,17] Cycle 1a crystallizes as a 1:1 complex with chloroform (Figure 1).<sup>[18]</sup> In contrast to inclusion complexes in which the chloroform molecule is stabilized through van der Waals interactions,<sup>[19]</sup> the guest in 1a is fully ordered. The hydrogen atom of chloroform points to the middle of a benzene ring, which leads to an unusual chloroform-arene hydrogen bond (distances  $C-\pi$ : 3.53 and 3.48 Å;  $H-\pi$ : 2.45 and 2.44 Å; angle C-H- $\pi$ : 171.2 and 159.2°, respectively, for the two molecules in the asymmetric units). This weak hydrogen bond is comparable to acetylenic CH hydrogen bonds.<sup>[20]</sup> The chloroform molecule is held in its position not only by this hydrogen bond but also by van der Waals interactions involving the chlorine atoms and the opposite benzene rings.

Suzuki cross-coupling is a feasible method for the gramscale synthesis of cyclic oligophenylenes. With the  $I/B(OH)_2$ substitution pattern, yields as high as 85% can be reproducibly obtained. In view of the considerable size of cycles **1**, it is not only the efficient coupling chemistry which is responsible for this high yield, but presumably also the rigid structure of

<sup>[\*]</sup> Prof. Dr. A.-D. Schlüter, Dipl.-Chem. V. Hensel, Dipl.-Chem. K. Lützow Institut für Organische Chemie der Freien Universität Takustrasse 3, D-14195 Berlin (Germany)
Fax: Int. code + (030) 838-3357 e-mail: adschlue@chemie.fu-berlin.de
Dipl.-Krist. J. Jacob, Dr. K. Gessler, Prof. W. Saenger Institut für Kristallographie der Freien Universität Berlin (Germany)
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