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as supplementary publication no. CCDC-100156. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code + (1223) 336-033; e-mail: deposit@chemcrys.cam.ac.uk).

- [15] a) SHELXS-86: G. M. Sheldrick, Acta Crystallogr. Sect. A 1990, 46, 467;
  b) SHELXL-93: G. M. Sheldrick, Universität Göttigen, 1993.
- [16] The Cambridge Crystallographic Database contains W-B bond lengths between 2.170 and 2.557 Å.
- [17] H. Braunschweig, B. Ganter, M. Koster, T. Wagner, Chem. Ber. 1996, 129, 1099.
- [18] The proton-decoupled <sup>13</sup>C NMR spectrum of **6b** contains a triplet with J(C,H) = 115 Hz due to the methylene group of the benzyl ligand. Therefore **6b** does not differ substantially from normal alkylboranes in that respect, although a reduction in the C-H coupling constant would be expected for an agostic methylene group. Due to the fast exchange between the two methylene protons however, the value obtained is an average of the <sup>13</sup>C-<sup>1</sup>H coupling constants of the terminal and agostic protons. The relatively large value can be explained by the usual increase in <sup>1</sup>J(C,H(terminal)) when <sup>1</sup>J(C,H(agostic)) becomes smaller[19]; this has been experimentally verified for the carbene complexes 7[20]. The obvious comparison with the signal of the methylene group of the nonagostic thyl group in **6** is not possible due to overlap with the methyl signals.
- [19] M. Brookhart, M. L. H. Green, J. Organomet. Chem. 1983, 250, 395.
- [20] S. G. Feng, P. S. White, J. L. Templeton, J. Am. Chem. Soc. 1990, 112, 8192; ibid. 1992, 114, 2951.
- [21] J. Emsley, The Elements, 2nd ed., Clarendon, Oxford, 1991.
- [22] N. M. Kostic, R. F. Fenske, Organometallics 1982, 1, 974.
- [23] M. D. Curtis, K.-B. Shiu, W. M. Butler, J. C. Huffman, J. Am. Chem. Soc. 1986, 108, 3335.
- [24] We would like to thank a referee for pointing out that the boryl complexes 5 and 6 could also be produced by the addition of "Et<sub>2</sub>BH", which is more reactive than "EtBH<sub>2</sub>" (extrusion of BEt<sub>3</sub> from an intermediate). Our observation that (PhBH<sub>2</sub>)<sub>2</sub> reacts with 4b to yield the corresponding agostic complex [(tpb)(CO)<sub>2</sub>WB(Ph)CH<sub>2</sub>-p-tolyl) under milder conditions (room temperature) and faster (<5 min) would tend to indicate that this is not the case here.
- [25] R. J. Kazlauskas, M. S. Wrighton, J. Am. Chem. Soc. 1982, 104, 6005.
- [26] The photochemical cleavage of CO from matrix-isolated  $[(C_sMe_s)(CO)_3-W(C_2H_s)]$  leads via several intermediates to 10[25]. We observed magnetization transfer between the hydridic and olefinic protons in 10 [10b] by NMR spectroscopy. This can be explained by a dynamic equilibrium between 10 and 11.
- [27] J. C. Jefferey, F. G. A. Stone, G. K. Williams, Polyhedron 1991, 10, 215.
- [28] R. Köster, P. Binger, Inorg. Synth. 1974, 15, 142.

# Mechanistic Insights into the Very Efficient [ReO<sub>3</sub>OSiR<sub>3</sub>]-Catalyzed Isomerization of Allyl Alcohols

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Dedicated to the late Geoffrey Wilkinson, mentor, inspirer, and friend

The isomerization of allyl alcohols by the 1,3 transposition of an hydroxy group (Scheme 1 a) is catalyzed by certain high oxidation state transition metal oxo complexes, and has been carried out industrially by using [VO(OR)<sub>3</sub>] or [WO(OR)<sub>4</sub>] catalysts at high temperatures (ca. 130–200 °C) for the production of terpenic alcohols.<sup>[1]</sup> Recently Mo and V catalysts have been reported<sup>[2, 3]</sup> that are active at 25 °C. However, we find that in the case of the MoO<sub>2</sub>X<sub>2</sub> complexes (X = Cl, OtBu), slow reduction of the Mo<sup>VI</sup> center by the alcohol takes place,<sup>[3]</sup> thereby causing a loss of catalytic activity with time. Based on these observations we have developed dioxomolybdenum(VI) catalysts that under appropriate conditions oxidize allyl and benzyl alcohols selectively to aldehydes.<sup>[4]</sup>

The proposed mechanism of the isomerization process, however, is still largely dependent on the original insight of Charbardes et al.,<sup>[1]</sup> and involves a cyclic transition state (Scheme 1 b), akin to that of a Claisen type rearrangement, incorporating a metal oxo unit. Further, we have proposed<sup>[3]</sup> that



Scheme 1. Catalytic isomerization of allyl alcohols (a) and the proposed cyclic transition state (b).

the efficiency of the  $[MoO_2(OR)_2]$  catalysts results, in part, from the second oxo group serving as a spectator ligand,<sup>[5]</sup> helping to stabilize negative charge developed on the metal in the transition state, thereby lowering the activation barrier for the rearrangement. We reasoned that a further increase in the number of oxo ligands around the metal may lead to an even greater stabilization of the charge and thus a more active catalyst system. We present here some catalytic studies on the trioxorhenium complexes [ReO<sub>3</sub>(OSiR<sub>3</sub>)] 1 (R = Me<sup>[6]</sup>) and 2 (R = Ph<sup>[7]</sup>), which we found are by far the most efficient catalysts yet known for this isomerization reaction, and thereby have allowed us to obtain further details on the mechanism. Additionally these complexes are considerably more stable towards reduction, giving long-lived catalysts.

For example, using  $2.2 \times 10^{-2}$  M of the rhenium catalyst 1 in acetonitrile at 25 °C, 50 equivalents of hex-1-en-3-ol are isomerized at an initial rate  $(v_i)$  of 8 turnovers per min (graphically determined by extrapolation to initial time); the equilibrium<sup>[8]</sup> with trans-hex-2-en-1-ol is reached in less than 10 minutes. This rate is over 10<sup>2</sup> times higher than that observed for the previously described dioxomolybdenum(vi) catalyzed systems under similar conditions which require about 24 h to reach this equilibrium. Even at 0 °C  $v_i$  with 1 is 2.5 turnovers per min. The analogous triphenylsiloxy derivative 2 is found to be even more active ( $v_i > 10$  turnovers per min at 0 °C; equilibrium is reached in about 5 min). In contrast to the molybdenum catalysts, no degradation of these rhenium systems is observed over 50 h. Further, using 1 and 2-methylbut-3-en-2-ol as substrate, equilibrium with 3-methylbut-2-en-1-ol is obtained in 2 min at 22 °C but, in contrast to the molybdenum catalysts, no concomitant diallyl ether formation is observed.<sup>[9]</sup> Only after leaving the products in contact with the catalyst over a further two hours are such ethers detectable.

The greater catalytic activity of 2 in comparison to that of 1 results from inhibition caused by the formation of water when 1 is used. <sup>1</sup>H NMR, studies show that, as expected, the allyl alcohol substrate displaces the  $R_3$ SiOH from 1 and 2 but unlike triphenylsilanol, trimethylsilanol condenses rapidly to form hexamethyldisiloxane and water. Indeed, addition of small quantities of water was found to inhibit the catalytic process,

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Figure 1. Conversion of A into B and C in  $CH_2Cl_2$  at 6 °C (proportion x [%] of the alcohol in the course of the reaction determined by gas chomatography). Catalyst:  $2,[2] = 4.4 \times 10^{-3} \text{ mol } L^{-1}$ , 100 equiv of substrate.

presumably the water competes with the alcohol substrate for a metal binding site leading to the formation of perrhenic acid. The  $(Bu_4N)[ReO_4]/p$ -TsOH combination also catalyzes such isomerizations, but activities were found to be at least an order of magnitude inferior to those reported here and moreover, extensive dehydration of secondary and tertiary alcohols was found to occur.<sup>[10]</sup>

Kinetic studies were carried out with 2 using each of the three hexenols separately as substrates, and the conversion of a given hexenol into the other two isomers was

monitored by gas chromatography (see Figure 1). The most striking observations are 1) the extremely low rate of formation of the cis-hex-2-en-1-ol (C)  $(v_i = 0.07)$ turnovers per min) compared with that of the trans-hex-2-en-1-ol (**B**)  $(v_i = 9.00)$ turnovers per min) in the catalyzed isomerization of hex-1-en-3-ol (A), and 2) the extremely slow conversion of the cis isomer into the other isomers ( $v_i = 0.16$ turnovers per min). We have measured the initial rate of isomerization at different concentrations of 2 and the substrate as well as at different temperatures and in several solvents. The kinetic dependence measured at 0 °C in CH<sub>2</sub>Cl<sub>2</sub> was found to be given by Equation (a) for all experi-

$$v_{i} = - d[substrate]/dt$$
  
= k[cat.]<sup>1</sup>[substrate]<sup>0</sup> (a)

ments. Consequently, in the presence of an excess of substrate, the kinetic dataare consistent with the rearrangement of the allyl moiety in the complex being the rate-determining step (Scheme 2, step II)

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and not the alcohol exchange step (Scheme 2, steps III and I).

Thermodynamic activation data were obtained from studies of the initial rates as a function of temperature (between 0°C and +30 °C). Hence for the formation of **B** from A,  $\Delta H_1^{\pm} = 13.3 \pm 0.3 \text{ kcal mol}^{-1}$  and  $\Delta S_1^{\pm} =$  $-14.8\pm1.0$  e.u., and for the reverse reaction  $\Delta H_{-1}^{\pm} = 12.4 \pm 0.6 \text{ kcal mol}^{-1}$  and  $\Delta S_{-1}^{\pm} =$  $-18.3\pm2.2$  e.u. The largely negative activation entropy  $\Delta S^*$  and the value of  $\Delta H^*$  are in agreement with the intervention of a cyclic transition state with some charge separation, that is with a partially positively charged allyl group migrating intramolecularly across a partially negatively charged perrhenate moiety. However, for the slow formation of C from A, and its reverse reaction, rather higher activation enthalpies ( $\Delta H_2^* = 20.9 \pm 0.4$  and  $\Delta H_{-2}^{+} = 24.9 \pm 0.7 \text{ kcal mol}^{-1}$ ) and positive activation entropy values  $(\Delta S_2^* = 3.1 \pm 1.5 \text{ e.u.})$  and  $\Delta S_{-2}^* = 19.3 \pm 2.2 \text{ e.u.})$  are found. The higher enthalpy values would appear to indicate a greater charge difference and/or separation (distance effect) in the transition state involving the cis-hexenol rearrangement; indeed, when more polar solvents are used for the hex-1-en-3-ol rearrangement, the increase in rate of forma-

tion of *cis*-hexenol is notably relatively greater than that of *trans*-hexenol. The unexpected positive entropy of activation for the *cis*-hexenol case may result from a quasi-ionic pair transition state, in which the highly positively charged allyl group is well separated from the perrhenate moiety. The reason for this increase in charge separation is unclear. On supposing a cyclohexane-like transition state (Scheme 1), a *trans*-axial interaction between an oxo ligand and the propyl substituent on the migrating allyl group, which will be greater for the *cis* isomer, may



Scheme 2. Proposed mechanism of the [ReO3(OSiR3)]-catalyzed isomerization of allyl alcohols

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enforce an increase in the charge separation. However, whether an oxo ligand is sufficiently voluminous to have this steric effect is debatable, and calculations are currently underway to resolve this question.<sup>[11]</sup> Although the greater thermodynamic stability of the *trans* alcohol with respect to that of the *cis* isomer (ca. 1.5 kcalmol<sup>-1</sup>) could lead to a relative lowering of the transition state free energy (invoking the Hammond postulate), it would be insufficient to account for these effects. Interestingly, in the thermal gas phase rearrangements of allyl esters,<sup>[12]</sup> in which a similar mechanism involving an allyl migration process is postulated, the *cis* product was also found to be formed at a considerably lower rate than the *trans* isomer.

Overall these results are in good agreement with the model proposed by Charbardes et al., which, however, must be modulated by some rather subtle effects in the charge distribution in the cyclic transition state and its effects on selectivity. It appears that the type of bond formed between the allyl fragment and the perrhenium fragment in the transition state may vary greatly from ionic–covalent to nearly totally ionic.<sup>[13]</sup> Finally, given the very high activity of these rhenium catalysts under mild conditions, urther modification of the ligand environment, for example by replacing oxo ligands with imido groups, would appear to offer the prospect of both greater catalyst control and selectivity in rearrangements of this type.

> Received: November 8, 1996 [Z 9773IE] German version: Angew. Chem. 1997, 109, 1011~1013

**Keywords:** allyl alcohols  $\cdot$  homogeneous catalysis  $\cdot$  isomerizations  $\cdot$  O ligands  $\cdot$  rhenium

- a) P. Chabardes, E. Kuntz, J. Varagnat, *Tetrahedron* 1977, 33, 1775; b) G. W. Parshall, S. D. Ittel, *Homogeneous Catalysis*, 2nd ed., Wiley Interscience, New York, 1992, p. 19.
- [2] a) T. Hosogai, Y. Fujita, Y. Ninagawa, T. Nishida, Chem. Lett. 1982, 357; b) S. Matsubara, T. Okazoe, K. Oshima, K. Takai, H. Nozaki, Bull. Chem. Soc. Jpn. 1985, 58, 844.
- [3] a) J. Belgacem, J. Kress, J. A. Osborn, J. Am. Chem. Soc. 1992, 114, 1501; b) J. Belgacem, J. Kress, J. A. Osborn, J. Mol. Catal. 1994, 86, 267.
- [4] C. Y. Lorber, I. Pauls, J. A. Osborn, Bull. Chim. Soc. Fr. 1996, 133, 755.
- [5] A. K. Rappé, W. A. Goddard, III, J. Am. Chem. Soc. 1982, 104, 448.
- [6] M. Schmidt, H. Schmidbaur, Inorg. Synth. 1967, 9, 149.
- [7] T. Schoop, H. W. Roesky, M. Noltemeyer, H. G. Schmidt, Organometallics 1993, 12, 571.
- [8] Total equilibrium of the three isomers has not been strictly obtained at this time since the isomeric cis alcohol is still far from equilibrium. However, the ratio of the concentration of the *trans* isomer to that of hex-1-en-3-ol after 10 mins remains essentially constant at the final equilibrium value.
- [9] See also: J. M. Brégeault, B. El Ali, J. Martin, C. Martin, F. Derdar, G. Bugli, M. Delamar, J. Mol. Catal. 1988, 46, 37.
- [10] K. Narasaka, H. Kusama, Y. Hiyashi, Chem. Lett. 1991, 1413.
- [11] A. Dedieu, S. Bellemin-Laponnaz, J. P. Le Ny, J. A. Osborn, unpublished results.
- [12] E. S. Lewis, J. T. Hill, E. R. Newman, J. Am. Chem. Soc. 1968, 90, 662.
- [13] See also: D. M. T. Chan, W. A. Nugent, Inorg. Chem. 1985, 24, 1424.

## $[H_3N(CH_2)_2NH_3]_{0.5}^{2+}[Sn_4P_3O_{12}]^-:$ An Open-Framework Tin(11) Phosphate\*\*

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The ever-growing family of microporous aluminophosphates, first reported in 1982 by Flanigen et al.,<sup>[1]</sup> continues to stimulate interest in the synthesis of other phosphate compounds with open-framework structures. More recent examples include the aluminophosphate DAF-1 (two 12-ring channel system),<sup>[2]</sup> the gallophosphate cloverite (20-membered ring opening),<sup>[3]</sup> and a number of zinc<sup>[4]</sup> and indium phosphates.<sup>[5, 6]</sup> In addition, the rich chemistry of molybdenum and vanadium has been exploited in the synthesis of a variety of similar materials with interesting architectures.<sup>[7-10]</sup> It is now clear that judicious choice of reaction conditions (such as gel composition, structure-directing agent, and temperature) is necessary for synthesizing new compounds with open-framework structures. We are currently studying the tin/phosphorus system.

Small concentrations of tin can be substituted into the framework of aluminosilicates.[11-14] These materials find use as adsorbents,<sup>[11]</sup> ionic conductors,<sup>[12]</sup> and catalysts.<sup>[13]</sup> A large number of dense tin phosphates are known to exist,<sup>[15-21]</sup> of which most contain Sn<sup>IV</sup>, [15-17] and only a few Sn<sup>II</sup> [18-21] However, we are not aware of any open-framework structures based on tin phosphate. The challenge of synthesizing such a compound with tin in the oxidation state II is all the more interesting because of the lone pair on Sn<sup>II</sup>. Sn<sup>II</sup> compounds often adopt layered structures in which the lone pairs are perpendicular to the plane of the layers. Three-dimensional, open-framework structures would be promising materials as catalyts with Sn<sup>II</sup> as a redox center or a host for base-catalyzed chemical reactions. In addition, open-framework structures offer higher stability and accessibility to guest molelcules than layered materials, which often require post-synthetic treatment such as pillaring to enhance these properties. Here, we report the synthesis and structure of en-SnPO-1, the first compound with an openframework structure based on tin phosphate.

Colorless en-SnPO-1 crystallizes in the orthorhombic space group *Pnaa* (see Experimental Section). The structure is based on a network of strictly alternating pyramidal SnO<sub>3</sub> and tetrahedral PO<sub>4</sub> moieties, in which all the vertices are shared; the framework has the formula  $[Sn_4P_3O_{12}]^-$ . Charge neutrality is achieved by incorporation of the organic template ethylenediamine (en) in its diprotonated form: there are 0.5  $[H_2en]^{2+}$ ions per framework formula unit.

The asymmetric unit of *en*-SnPO-1 contains 21 non-hydrogen atoms (Figure 1a). The framework is constructed from cages containing four eight-membered rings that are linked to form four sides of a cube. The other two faces of the cube consist of a six-membered ring and two edge-sharing, four-membered rings (Figure 1b). The protonated en molecules sit inside these cages on a twofold rotation axis along c. The cages are stacked to form an eight-ring channel, in which alternating cages are rotated by 90° (Figure 1c). Four of these channels are connected to each other to define a second channel with squashed twenty-

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<sup>[\*\*]</sup> The work was funded by the MRSEC program of the U.S. National Science Foundation (DMR 9632716).