Amide/Hydride Transformation

DIBAH-Mediated Amide/Hydride Transformation in *ansa*-Lanthanidocene(III) Complexes**

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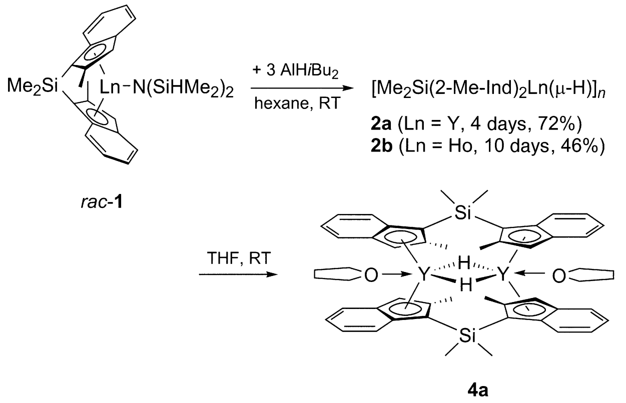
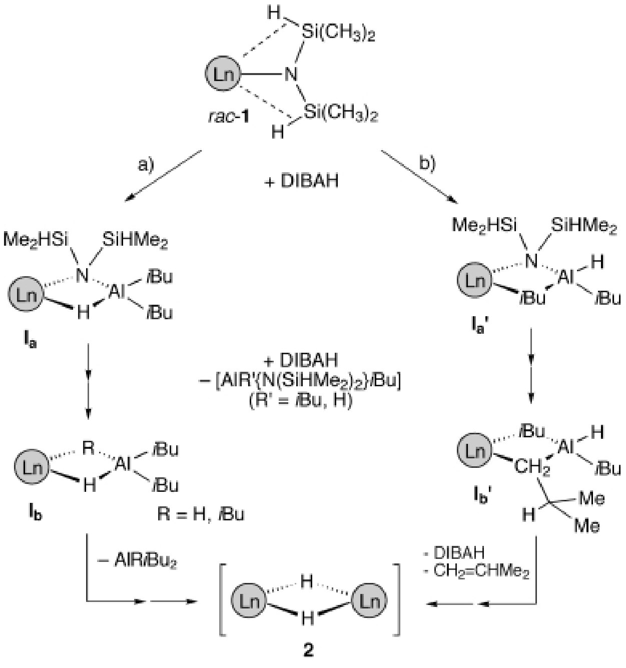
Lanthanidocene(III) hydride derivatives are classified as highly efficient precatalysts for a variety of olefinic transformations,[1] such as the polymerization of ethylene[2] and methylmethacrylate[3] as well as hydrogenation[4] and hydrosilylation reactions.[5] Such highly reactive discrete molecular hydride complexes are commonly synthesized, both on a preparative scale or in situ, by hydrogenolysis of lanthanidocene alkyl complexes.[6] Less cumbersome synthetic routes comprise: a) thermal decomposition[7] or silanolysis of alkyl derivatives,[8] b) salt metathesis of lanthanidocene(III) chloride complexes with NaH or $LiAlH_4$,[9,10] and c) oxidation of samarocene(II) complexes with $AlH_3(NEt_3)$.[11] Recently, we applied an "extended silylamide route"[12] to generate heteroleptic lanthanidocene(III) bis(dimethylsilyl)amide complexes, including the first Brintzinger-type, indenyl-derived *ansa*-lanthanidocene derivatives.[13] Here we report that the silylamide moiety in *rac*-$[\{Me_2Si(2\text{-}Me\text{-}C_9H_5)_2\}Ln\{N(SiHMe_2)_2\}]$ (Ln = Y, Ho) can be easily hydrogenated with diisobutylaluminumhydride (DIBAH). Although the hydrogenating power of DIBAH is well-established in organic synthesis,[14] it has been scarcely used as a hydrogenating reagent in organometallic chemistry.[15]

Inspired by the ease of the $[N(SiHMe_2)_2]\rightarrow[AlR_4]$ transformation which occurs in the reaction of rare earth metal silylamide complexes with an excess of trialkylaluminum reagents,[16] we were intrigued by the feasibility of other $[N(SiHMe_2)_2]\rightarrow[X]$ transformations by exploiting the formation of a thermodynamically very stable Al–N bond. Accordingly, a suspension of *rac*-$[\{Me_2Si(2\text{-}Me\text{-}C_9H_5)_2\}Y\{N(SiHMe_2)_2\}]$ (*rac*-**1a**) in *n*-hexane was treated with an excess (3 equiv) of a commercially available sample of DIBAH (Scheme 1). The initially formed clear solution gradually produced a pale yellow precipitate. After four days, the yield of the hydrogenated species **2a** was 72 %.



Scheme 1. Synthesis of **2** and **4a**. Only one enantiomer of *rac*-**1a** is depicted.

Both microanalytical (no nitrogen detected) and IR spectroscopic data (disappearance of the characteristic silylamide vibration $\tilde{\nu}(SiH)$ at 1804 cm^{-1}) were indicative of the formation of a hydrogenated product. The recording of NMR spectra of yttrium complex **2a** was hampered by its low solubility in aliphatic and aromatic hydrocarbons. However, additional preparative investigations provided important details of the mechanism of the $[N(SiHMe_2)_2]\rightarrow[H]$ transformation. The proposed reaction sequence is shown in Scheme 2a. Initial formation of heterobimetallic complex *rac*-$[\{Me_2Si(2\text{-}Me\text{-}C_9H_5)_2\}Y\{\mu\text{-}N(SiHMe_2)_2\}(\mu\text{-}H)Al\textit{i}Bu_2]$ as reaction intermediate $\mathbf{I}_a$ is plausible since similar Lewis acid/base adducts have been isolated in the form of homoleptic complexes such as $[Yb\{N(SiMe_3)_2\}_2(AlMe_3)_2]$.[17] Additionally, a bridging mode of the small hydride ligand should be favored compared with a bridging isobutyl group (as in $\mathbf{I}_a'$) for



Scheme 2. Proposed reaction pathways for the formation of hydride dimer **2**.

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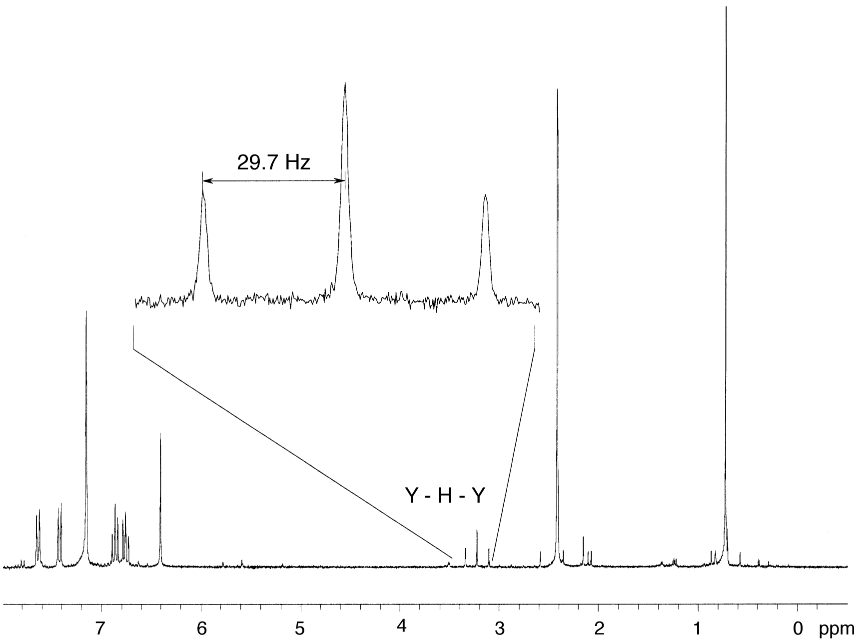

Figure 1. ^{1}H NMR spectrum of **4a** recorded in $\mathrm{C_6D_6}$ at 25 °C.

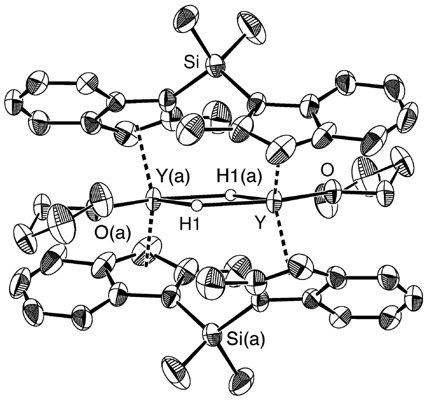

Figure 2. PLATON drawing of complex **4a**. Atoms are represented by atomic displacement ellipsoids at the 50% level. Except for the bridging H and H(a) atoms, all hydrogen atoms are omitted for clarity. For selected bond lengths and angles see Table 1.

steric and thermodynamic reasons (Scheme 2b).[18,19] Steric considerations also suggest that the formation of intermediate $\mathbf{I}_\mathrm{a}$ is the rate-determining step. In the present system, intermediate $\mathbf{I}_\mathrm{a}$ could not be isolated, and was most likely converted via intermediate $\mathbf{I}_\mathrm{b}$ into the kinetically favored hydride complex **2**. The second intermediate $\mathbf{I}_\mathrm{b}$ is formed upon interaction of $\mathbf{I}_\mathrm{a}$ with additional DIBAH. In accordance with this scenario is the exclusive formation of **2** along with recovered *rac*-**1a** from an equimolar reaction of *rac*-**1a** with DIBAH, as shown in Scheme 1. Moreover, intermediate $\mathbf{I}_\mathrm{b}$ with R = *i*Bu could be isolated as the only stable reaction product ($[(\mathrm{Ph_4C_5H})_2\mathrm{La}(\mu\text{-H})(\mu\text{-}i\mathrm{Bu})\mathrm{Al}i\mathrm{Bu}_2]$ (**3**)) from the reaction of sterically highly encumbered $[(\mathrm{Ph_4C_5H})_2\mathrm{La}\{\mathrm{N(SiHMe_2)_2}\}]$[20] with two equivalents of DIBAH. The presence of a bridging hydride ligand in complex **3** is clearly visible in the ^{1}H NMR spectrum at $\delta = 5.19$ ppm ($\delta(\mathrm{H_{DIBAH}}) = 3.05$ ppm). Finally, rapid conversion of intermediate $\mathbf{I}_\mathrm{b}$ into the bridged hydride complex **2** most likely proceeds by dissociation of weakly coordinated $\mathrm{AlR}i\mathrm{Bu}_2$ (R = H, *i*Bu) and irreversible dimerization of mononuclear metallocene hydride units (which precipitate from hexane and toluene); intermediate $\mathbf{I}_\mathrm{b}$ is not formed, however, in the presence of a large excess of $\mathrm{Al}i\mathrm{Bu}_3$. Formation of lanthanide hydride complex **2** by β-H-elimination of a doubly *i*Bu-bridged intermediate $\mathbf{I}_\mathrm{b}'$ would be an optional reaction pathway.[7] The availability of two μ-*i*Bu groups in lanthanidocene complexes was recently evidenced for $[\mathrm{Cp}^*_2\mathrm{Sm}(\mu\text{-}i\mathrm{Bu})_2\mathrm{Al}i\mathrm{Bu}_2]$ and *rac*-$[\{\mathrm{Me_2Si(2\text{-}Me\text{-}C_9H_5)_2}\}\mathrm{Y}(\mu\text{-}i\mathrm{Bu})_2\mathrm{Al}i\mathrm{Bu}_2]$.[21,22] The involvement of *ansa*-ligand rearrangement (see below) might further complicate such a DIBAH-mediated $[\mathrm{N(SiHMe_2)_2}]\rightarrow[\mathrm{H}]$ transformation.[23,24] The strong dependency of the reaction on stereoelectronic factors could be further demonstrated by the isolation of **2b** containing the similarly sized holmium center, while the corresponding lutetium derivative did not form under these conditions.

Complex **2a** readily dissolves in benzene on addition of a small amount of a donor solvent such as tetrahydrofuran and yields complex **4a** (Scheme 1). The formulation of **4a** as a symmetrically bridged hydride dimer is based on the 1:2:1 triplet structure of the bridging hydride ligands at $\delta = 3.22$ ppm in the ^{1}H NMR spectrum (Figure 1; two equivalent ^{89}Y nuclei, $^1J_\mathrm{YH} = 29.7$ Hz).[25]

An X-ray structure analysis of complex **4a**[26] revealed the presence of a "flyover dimer"[23] of composition $[\{\mathrm{Y(thf)}\}_2\{\mu_2\text{-}[(\eta^5\text{-2-Me-C_9H_5})\mathrm{SiMe_2}(\eta^5\text{-2-Me-C_9H_5})]\}_2(\mu_2\text{-H})_2]$ as the predominant structural motif (Scheme 1, Figure 2). It is known that single-atom-linked *ansa*-lanthanidocene complexes tend to abandon the chelating "wedge-type" binding mode (as shown for *rac*-**1** in Scheme 1) in favor of this "spanning" coordination mode. Structurally characterized examples featuring this binding mode comprise $[\{\mathrm{Me_2Si(C_5H_4)_2Yb}\text{-}(\mu\text{-Cl})\}_2]$,[27a] $[\{\mathrm{Me_2Si(C_5H_4)_2Yb}\}_2(\mu\text{-H})(\mu\text{-Cl})]$,[27b] $[\{\mathrm{Et_2Si(C_5H_4)(3,4\text{-}Me_2\text{-}C_5H_2)Lu}(\mu\text{-H})\}_2]$ (**5**),[24] $[\{\mathrm{Et_2Si(C_5H_4)(3,4\text{-}Me_2\text{-}C_5H_2)Lu}\}_2(\mu\text{-H})(\mu\text{-Et})]$,[24] and $[\{\mathrm{Me_2Si(3\text{-}SiMe_3\text{-}C_5H_3)_2Sm(thf)}(\mu\text{-H})\}_2]$ (**6**).[3a] The spanning mode is particularly favored in the presence of small ligands such as H or Cl and sterically demanding linked cyclopentadienyl ligands.

Table 1 summarizes selected bond lengths and angles by comparing those of complex **4a** with the relevant "flyover" dimers **5** and **6**. The bonding parameters of the $\{\mathrm{Ln}(\mu\text{-H})_2\mathrm{Ln}\}$ core respond extremely sensitively to repulsive metal···metal interactions, that is, they are sensitive to the metal size. The Y···Y distances and Y−H bond lengths of **4a** fall in the range of those observed in other dimeric hydrido complexes,[6,28–33] for example, $[\{(\mathrm{Me\text{-}C_5H_4})_2\mathrm{Y(thf)}(\mu\text{-H})\}_2]$ (3.66(1); 2.17(8), 2.19(8) Å),[6] $[\{(1,3\text{-}\mathrm{Me_2\text{-}C_5H_3})_2\mathrm{Y(thf)}(\mu\text{-H})\}_2]$ (3.68(1); 2.03(7), 2.27(6) Å),[28] $[\{(2,4,7\text{-}\mathrm{Me_3C_9H_4})_2\mathrm{Y}(\mu\text{-H})\}_2]$ (2.09(4)–2.14(7) Å),[29] $[\{\mathrm{SiMe_2(C_5Me_4)(NCMe_3)Y(thf)}(\mu\text{-H})\}_2]$ (3.672(1); 1.98(6)–2.48(4) Å),[30] $[\{[\mathrm{PhC(NSiMe_3)_2}]_2\mathrm{Y}(\mu\text{-H})\}_2]$

Table 1: Selected structural parameters in "flyover" lanthanidocene hydride complexes [{$Me_2Si(2\text{-}Me\text{-}C_9H_5)_2Y(thf)(\mu\text{-}H)$}$_2$] (**4a**), [{$Et_2Si(C_5H_4)(3,4\text{-}Me_2\text{-}C_5H_2)Lu(\mu\text{-}H)$}$_2$] (**5**), and [{$Me_2Si(3\text{-}SiMe_3\text{-}C_5H_3)_2Sm(thf)(\mu\text{-}H)$}$_2$] (**6**).

Feature[a]	**4a** (Ln = Y)	**5** (Ln = Lu)[24]	**6** (Ln = Sm)[3a]
	Bond lengths [Å]		
Ln(1)···Ln(1a)	3.6524(3)	3.390(1)	3.762(1)
Ln–C_g(1)	2.480(1)	2.27	2.46
Ln–C_g(2)	2.447(2)	2.29	2.48
Ln–C(range)	2.656(3)–2.844(3)	2.551(4)–2.608(4)	2.706(7)–2.813(7)
Ln–H(1)	2.09(3)	2.15(4)	1.91
Ln–H(1a)	2.13(3)	2.12(4)	2.15
	Bond angles [°]		
C_g(1)-Ln-C_g(2)	127.51(5)	130.2	132.4
H(1)-Ln-H(1a)	60(1)	75.2	39
Ln(1)-H(1)-Ln(1a)	120(1)	104.8	141

[a] C_g(1) and C_g(2) = ring centroid. Ln–H bond lengths have to be discussed carefully because of the location of the hydrogen atoms close to two heavy atoms.

(2.11(3)–2.19(3) Å),[31] and [{(dadmb)Y(thf)(μ-H)}$_2$] (3.6652(8); 2.22(4), 2.27(4) Å (dadmb = 2,2′-bis-((*tert*-butyldimethylsilyl)amido)-6,6′-dimethylbiphenyl)).[32] The spanning geometry of the μ-[$Me_2Si(2\text{-}Me\text{-}C_9H_5)_2$] ligand results in the C-Si-C angle of 115.3(1)° in **4a** being markedly widened relative to that of synthetic precursor *rac*-**1a** (100.9(1)°).

These preliminary results show that *ansa*-lanthanidocene hydride derivatives can be synthesized by treatment of the silylamide precursor with DIBAH at ambient temperature. We are currently examining the scope of DIBAH-mediated amide/hydride transformation reactions in organolanthanide and early transition metal chemistry.

Experimental Section

Representative syntheses of **2a** and **4a**: A 1M solution of diisobutylaluminumhydride (3 equiv) in *n*-hexane was added to a suspension of *rac*-**1a** (535 mg, 1.00 mmol) in *n*-hexane (10 mL) at ambient temperature in an argon-filled glovebox. The lemon yellow suspension immediately became a pale yellow solution and after about 5 min a pale yellow precipitate formed. The reaction mixture was then stirred for 4 days at ambient temperature. The suspension was then centrifuged and the residue washed twice with *n*-hexane (5 mL) and dried in high vacuum to leave **2a** as a pale yellow powder (292 mg, 72 %). Complex **4a** was obtained upon addition of a small amount of THF to a suspension of **2a** in benzene. Colorless prisms of **4a** suitable for X-ray analysis were obtained from a saturated benzene solution at ambient temperature. IR (nujol) of **2a**: $\tilde{\nu}$ = 1351 s, 1276 s, 1201 s, 1036 m, 874 m, 834 m, 806 m, 773 m, 737 s, 641 w, 461 w, 427 m cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 25 °C) of **4a**: δ = 7.66 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, indenyl), 7.54 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, indenyl), 6.81 (dd, 2 × $^3J_{H,H}$ = 7.3 Hz, 2 H, indenyl), 6.72 (dd, 2 × $^3J_{H,H}$ = 8.4 Hz, 2 H, indenyl), 6.52 (s, 2 H, indenyl), 3.22 (t, $^1J_{Y,H}$ = 29.7 Hz, 1 H, Y-H-Y), 2.45 (s, 6 H, indenyl-CH_3), 0.71 ppm (s, 6 H, $Si(CH_3)_2$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 25 °C) of **4a**: δ = 140.3, 124.0, 123.6, 122.8, 121.4, 120.9, 120.1, 106.6, 105.4 (s, indenyl-C), 19.2 (s, indenyl-CH_3), 4.2 ppm (s, $Si(CH_3)_2$). Elemental analysis calcd for $C_{22}H_{23}SiY$ (**2a**): C 65.34, H 5.73; found: C 64.50, H 6.20. Full experimental and spectroscopic details for complexes **2b** and **3** are available in the Supporting Information.

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[25] A comprehensive survey of the ^{1}H NMR chemical shifts ($\delta = 1.85\text{–}8.31$ ppm) and ^{89}Y-^{1}H coupling constants (23.8–35.3 Hz) of dimeric yttrium hydrido complexes is presented in: K. C. Hultzsch, P. Voth, K. Beckerle, T. P. Spaniol, J. Okuda, *Organometallics* **2000**, *19*, 228.

[26] Compound **4a** ($C_{52}H_{62}O_2Si_2Y_2 \cdot 2\,C_6D_6$) crystallizes from benzene in the monoclinic space group $P2_1/c$ with $a = 11.7875(2)$, $b = 14.0396(3)$, $c = 16.8378(4)$ Å, $\beta = 104.2053(12)°$, $V = 2701.31(10)$ Å^3, and $\rho_{calcd} = 1.364\ \mathrm{g\,cm^{-3}}$ for $Z = 2$. Data were collected at 193 K on a Nonius Kappa-CCD system. The structure was solved by Patterson methods, and least-square refinement of the model based on 3682 reflections ($I > 2.0\sigma(I)$) converged to a final $R1 = 4.0\,\%$ ($wR2 = 8.1\,\%$). Except H(1), all hydrogen atoms were placed in calculated positions. H(1) was located in difference Fourier maps and refined with isotropic thermal parameters. CCDC-188842 (**4a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Photocatalytic Oxidation

An Efficient and Selective Photocatalytic System for the Oxidation of Sulfides to Sulfoxides**

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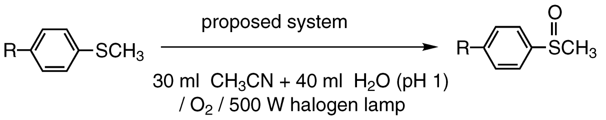
The selective oxidation of organic sulfides to sulfoxides without any overoxidation to sulfones is a challenging research interest in synthetic organic chemistry, partly because of the importance of sulfoxides as intermediates in biologically active compounds.[1] Of the many classical oxidants, H_2O_2-based systems are considered to be relatively clean and free of pollution.[2] Nevertheless, under catalytic conditions, the choice of H_2O_2 conditions and the stoichiometry with respect to the catalyst are critical to the selectivity of the reaction. Herein, we report a novel heterogeneous photochemical system for the selective transformation of organic sulfides to sulfoxides in the presence of oxygen using a nafion membrane doped with a lead ruthenate pyrochlore (Pyc) catalyst and a $[Ru(bpy)_3]^{2+}$ photosensitizer (designated as $|NPyc^{x-}Ru(bpy)|$). Figure 1a illustrates the typical procedure for the incorporation of Pyc into a nafion membrane.[3] The membrane (5 × 5 cm) was first soaked with a mixture of Pb^{2+} and Ru^{3+} ions (1.5:1), which led to electrostatic exchange of ions into the hydrophilic sites of nafion. The precipitation of Pyc (designated as $|NPyc^{x-}|$) was done by treating the ion-exchanged membrane in 1.1 M KOH at 53 °C for 24 h with continuous purging of O_2.[3a] The formation of Pyc was confirmed by X-ray diffraction analysis.[3a] The $|NPyc^{x-}|$ membrane was found to be highly stable in organic media.[4] Finally, a suitable amount of $[Ru(bpy)_3]^{2+}$ was doped into the $|NPyc^{x-}|$ membrane simply by an ion-exchange process from a solution containing 1 mM $[Ru(bpy)_3]^{2+}$. This membrane (designated as $|NPyc^{x-}Ru(bpy)|$) was then used in organic syntheses. Very few photochemical reactions have so far been reported for the sulfide oxidation reaction (SOR), and all the cases resulted in a mixture of products from C–S bond breakage and overoxidation through radical combination reactions.[5] In the present study a clean reaction [Eq. (1)] occurs, and the controlled catalytic oxygen reduction reaction (ORR) to H_2O_2 at the Pyc active sites is essential to the SOR (see below).

 (1)

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