

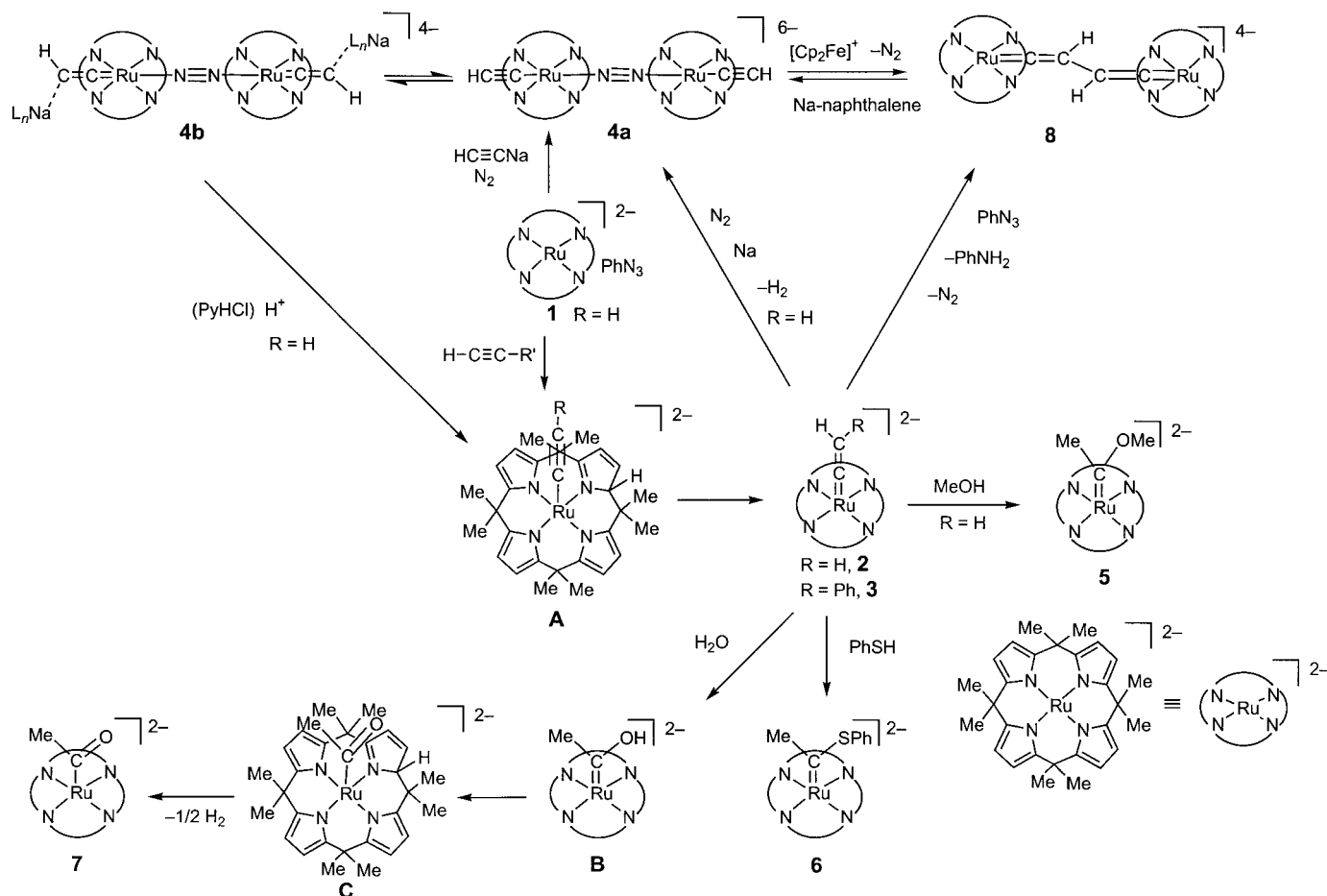
Acetylenes Rearranging on Ruthenium – Porphyrinogen and Leading to Vinylidene and Carbene Functionalities**

Lucia Bonomo, Christine Stern, Euro Solari, Rosario Scopelliti, and Carlo Floriani*

The *meso*-octaalkylporphyrinogen tetraanion^[1] has allowed the use of standard organometallic methodologies to be extended to a metalla-macrocycle, enabling the formation of unusual functionalities and the discovery of novel reactivities in a nonconventional organometallic environment. Herein we are specifically referring to the [Ru=C] group,^[2] which can be

found in a variety of forms throughout organometallic chemistry, and yet has a very limited presence in macrocyclic chemistry. This can be exemplified by the derivatization of Ru–porphyrin^[3] and Ru–tmtaa^[4] complexes (tmtaa = dibenzotetramethyltetraaza[14]annulene), where the Ru–carbene unit is produced from diazoalkanes^[3, 4] or by other methods.^[3c, 5]

Herein we report how we synthesized the [Ru=C=CHR] unit by acetylene rearrangements^[2, 6] in the reaction with **1** (see Scheme 1), and how we then converted the [Ru=C=CHR] unit into a variety of carbene and metal-lacumulene structures.^[2, 6] The paper most related to our work reports the reaction of Ru–porphyrin with ethyne to produce



Scheme 1. The synthesis and reactivity of the porphyrinogen–Ru–vinylidene functionality. Complexes **1**–**8** were isolated and fully characterized. Complexes **A**–**C** are speculative.

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a μ -biscarbene.^[7] Although these functionalities have various precedents in the case of cyclopentadienyl, phosphine, arene,^[2, 6, 8] and some amine^[9] ligands, they are absent in the macrocyclic ruthenium chemistry. The parent Ru-*meso*-octamethylporphyrinogen **1**^[10] was prepared according to the known procedure for this class of compounds.^[1] For the sake of clarity, compounds in Scheme 1 are reported in their anionic form, rather than in the ion-pair form usually identified in the solid state. Acetylene and phenylacetylene react smoothly with **1** to form **2** and **3**,^[10] respectively. Complexes **2** and **3** have been fully characterized, including the X-ray analysis of **2** (Ru=C 1.738(5), C=C 1.356(7) Å).^[2a]

Unlike in the reactions reported for the conventional Ru–organometallic fragments,^[2, 6, 8] the reaction discussed here, possibly, proceeds by a different pathway, which does not involve in a preliminary stage any η^2 complexation of the alkyne.^[11] Diphenylacetylene or other internal alkynes do not react with **1**. For **1**, we propose the preliminary protonation of the porphyrinogen skeleton^[12] followed by the binding of the acetylide anion to the metal (see intermediate **A** in Scheme 1), then rearrangement to the vinylidene functionality^[2, 6, 8] upon proton transfer from the porphyrinogen ligand. The protonation of Ni–porphyrinogen by $\text{PhC}\equiv\text{CH}$ ^[13] gave strong support to the hypothesis that the porphyrinogen ligand assists the proton transfer reaction; the reaction of **1** with $\text{CH}\equiv\text{CNa}$ in THF also supports this hypothesis. The reaction gave a compound which displays different structures in the solid state, depending on the crystallization solvent. The crystallization from dimethoxyethane (DME) led to **4a**, while the crystallization from THF gave the **4b** form. Both of these compounds contain the same core $[\{\text{Ru}(\text{Me}_8\text{N}_4)\}_2(\mu\text{-N}_2)(\mu\text{-Na})_4]^{2-}$, where the two Ru–porphyrinogen moieties are bridged by four sodium cations and a dinitrogen molecule.^[13] Although structural details are only given for **4b**, it is useful to stress the structural differences between **4a** and **4b**. The form **4a** contains the acetylide functionalities (Ru–C 1.875(3); C $\equiv$ C 1.185(4) Å) with two noninteracting sodium counteranions $[\text{Na}(\text{dme})_3]^+$, while in **4b** (see Figure 1),^[14] the terminal functionalities have the anionic vinylidene form, with the $[\text{Na}(\text{thf})_5]^+$ cations associated with them. In the latter case, the solvated sodium cation plays the role of an incoming electrophile (Ru=C 1.807(9), C=C 1.314(12) Å). Both forms **4a** and **4b**, when dissolved in $[\text{D}_8]\text{THF}$ ($\text{C}_4\text{D}_8\text{O}$), gave a ^1H NMR spectrum consistent with the **4b** structure. Complex **4b** in solution is easily protonated to **2**.

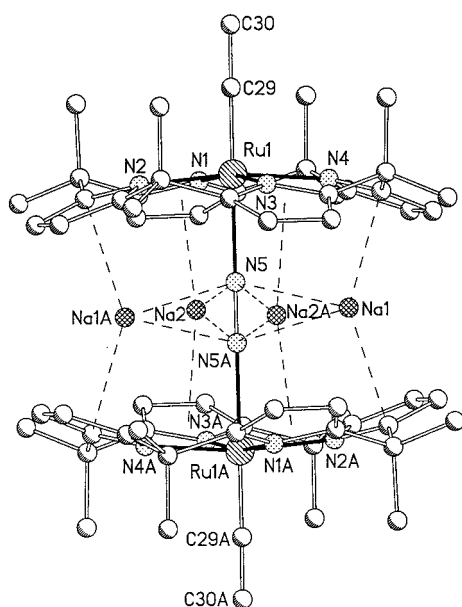


Figure 1. Molecular structure of **4b** (hydrogen atoms and $[\text{Na}(\text{thf})_5]^+$ ions are omitted for clarity). Selected distances [Å] and angles [°]: Ru1–N1– $\text{N}_{\text{average}}$ 2.119(8), Ru1–C29 1.807(9), Ru1–N5 2.251(8), C29–C30 1.314(12), N5–N5A 1.284(15), Na1...N5 2.573(10), Na1...N5A 2.609(9), Na2...N5 2.542(9), Na2...N5A 2.631(9); C29–Ru1–N5 179.2(4), N5A–N5–Ru1 177.4(10), C30–C29–Ru1 177.9(9). The A indicates the following symmetry operation: $-x+1, -y+1, -z+1$.

The vinylidene unit in **2** and **3** offers the synthetic entry to heterocarbenes and cumulenes otherwise inaccessible with macrocyclic ligands. Such synthetic versatility has been demonstrated in the reaction of **2** with methanol and thiophenol, leading to **5** and **6**, respectively.^[10] The reaction proceeds according to the vinylidene polarization with the proton reacting at the β carbon, followed by the nucleophile attacking the α carbon.^[2, 6] Unlike for many organometallic counterparts, the reaction occurs with a very high degree of selectivity and high yield. The characterization of **5** (Ru–C 1.80(1), C–OMe 1.38(1) Å) and **6** is given in the Supporting Information. The reaction of **2** with H_2O follows the pathway shown for the other protic substrates (Scheme 1, intermediates **B** and **C**),^[2, 6c] except that the final compound (**7**) has an acyl functionality which has been formed in conjunction with the oxidation of Ru^{II} to Ru^{III} , as depicted in Scheme 1. The complex is paramagnetic ($\mu_{\text{eff}} = 1.85$ BM at 293 K, $\tilde{\nu}_{\text{CO}} = 1577$ cm^{-1}), and has been characterized in the solid state by X-ray analysis (Ru–C 1.91(1), C=O 1.24(1) Å).

The vinylidene functionality in **2** allows a versatile derivatization of the Ru–porphyrinogen, thus providing an easy way to produce a dimetallabisvinylidene. The oxidation of **2** has been carried out using PhN_3 , which was reduced to aniline. The reaction led to **8**^[10] (Scheme 1; Ru–C 1.735(14), C–C 1.338(16), C–C 1.473(17) Å) by the oxidative coupling of the vinylidene functionality. The oxidation of **4b** using the oxidizing agent $[\text{Cp}_2\text{Fe}]^+$ gave **8** equally effectively (in solution **4a** converts into **4b**, see above). The latter reaction is reversible, since the reduction of **8** with Na–naphthalene gave back **4b** with the cleavage of a C–C single bond. The analytical and spectroscopic characterization of **8** is given in the Experimental Section while the X-ray structure, showing one out of the four sodium cations sandwiched between two porphyrinogen units, is displayed in Figure 2,^[14] the other

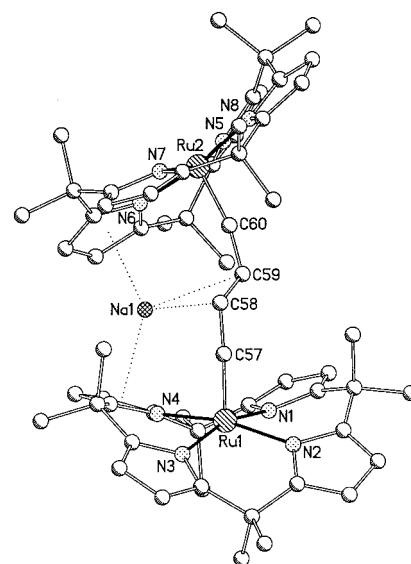


Figure 2. Molecular structure of compound **8** (hydrogen atoms, solvated sodium atoms, and solvent molecules are omitted for clarity). Selected distances [Å] and angles [°]: Ru1– $\text{N}_{\text{average}}$ 2.047(10), Ru1–C57 1.735(14), Ru2– N_{av} 2.033(12), Ru2–C60 1.734(14), C57–C58 1.338(16), C58–C59 1.473(17), C59–C60 1.326(17), Na1...C58 2.762(13), Na1...C59 2.796(14); C59–C60–Ru2 166.2(12), C58–C57–Ru1 164.6(11).

three sodium cations being present as solvent-separated cations. Complex **8** can provide an entry to dimetallacumulene and dimetallacarbene compounds.

Experimental Section

1: [RuCl₂(cod)] (6.19 g, 22.0 mmol; COD = 1.5 cyclooctadiene) was added to a solution of [Me₈N₄Na₄(thf)₄] (17.8 g, 22.0 mmol) in dimethoxyethane (DME; 300 mL). The reaction mixture was heated to reflux for 24 h and the NaCl was filtered off. The resulting solution was allowed to stand at –20 °C giving an orange crystalline product which was collected and dried in vacuo (11 g, 45 %). Crystals suitable for X-ray diffraction were grown in DME. ¹H NMR (400 MHz, [D₆]DMSO, 25 °C, TMS): δ = 5.74 (s, 8H; C₄H₂N), 3.41 (s, 24H; DME), 3.23 (s, 36H; DME), 1.43 (s, 24H; CH₃); ¹³C NMR (400 MHz, [D₆]DMSO, 25 °C): δ = 146.1, 100.1, 71.0, 58.0, 39.1, 36.9; elemental analysis calcd (%) for 1·6(C₄H₁₀O₂), C₅₂H₉₂N₄Na₂O₁₂Ru (1112.4): C 56.15, H 8.34, N 5.04; found: C 55.91, H 8.40, N 4.96.

2: A solution of 1·6(C₄H₁₀O₂) (1.50 g, 1.35 mmol) in THF (100 mL) was stirred under an acetylene atmosphere at room temperature for 24 h and then the solvent was removed in vacuo. The residue was treated with *n*-hexane (50 mL) giving an amber solid which was collected and dried in vacuo (0.93 g, yield 88 %). Crystals suitable for X-ray diffraction were grown in a mixture of THF/*n*-hexane. ¹H NMR (400 MHz, [D₆]benzene/[D₈]THF, 25 °C, TMS): δ = 6.46 (s, 8H; C₄H₂N), 3.06 (s, 8H; dimethoxyethane (DME)), 2.98 (s, 12H; DME), 2.78 (s, 2H; CH₂), 1.91 (s, 12H; CH₃), 1.81 (s, 12H; CH₃); ¹³C NMR (400 MHz, [D₆]benzene/[D₈]THF, 25 °C): δ = 300.28, 145.07, 102.44, 94.44, 71.51, 58.84, 39.49, 38.18, 33.21; IR (nujol, $\tilde{\nu}_{\text{max}}$): 1557.6 cm^{–1}; elemental analysis calcd (%) for 2·2(C₄H₁₀O₂), C₃₈H₅₄N₄Na₂O₄Ru (777.9): C 58.67, H 7.00, N 7.20; found: C 59.0, H 6.92, N 7.28.

4a:^[10] HC₂Na (86 mg, 1.8 mmol) was added to a solution of **1** (1.0 g, 0.9 mmol) in THF (100 mL) at room temperature. The reaction mixture immediately became light yellow. After 1 h of stirring, the solution was evaporated to dryness and the residue was washed with Et₂O (50 mL) to give a white solid which was collected and dried in vacuo (0.59 g, 77 %) (IR; $\tilde{\nu}_{\text{C}\equiv\text{C}}$, 2000 cm^{–1}). Crystals suitable for X-ray diffraction were grown in DME and have a different degree of solvation by THF than the noncrystalline product. ¹H NMR (400 MHz, [D₈]THF, 25 °C, TMS): δ = 5.76 (s, 8H; C₄H₂N), 5.68 (s, 8H; C₄H₂N), 3.47 (s, 24H; DME), 3.31 (s, 36H; DME), 2.19 (s, 2H; CH), 1.63 (s, 12H; CH₃), 1.58 (s, 12H; CH₃), 1.24 (s, 12H; CH₃), 1.18 (s, 12H; CH₃); elemental analysis calcd (%) for 4·6(C₄H₁₀O₂), C₆₄H₁₂₆N₁₀Na₆O₁₂Ru₂ (1808.0): C 55.80, H 7.02, N 7.75; found: C 55.85, H 7.05, N 7.67.

8: Method A: PhN₃ (0.61 mg, 5.14 mmol) was added to a solution of 2·2(C₄H₁₀O₂) (4.0 g, 5.14 mmol) in THF (100 mL). The reaction mixture was stirred at room temperature overnight, then evaporated to dryness and the solid residue triturated with *n*-hexane (100 mL) to give a brown solid which was collected and dried in vacuo (1.26 g, 85 %). Crystals suitable for X-ray diffraction were grown in a mixture of THF/dioxane. ¹H NMR (400 MHz, [D₅]pyridine, 25 °C, TMS): δ = 6.54 (s, 16H; C₄H₂N), 3.66 (s, 2H; CH), 3.48 (s, 16H; DME), 3.25 (s, 24H; DME), 1.90 (s, 24H; CH₃), 1.46 (s, 24H; CH₃); elemental analysis calcd (%) for 8·4(C₄H₁₀O₂), C₇₆H₁₀₆N₈Na₄O₈Ru₂ (1553.8): C 58.75, H 6.88, N 7.21; found: C 58.61, H 6.24, N 7.15. Method B: [Cp₂Fe]⁺BPh₄[–] (1.9 g, 3.38 mmol) was added to a solution of 4·4(C₄H₁₀O₂)·2(C₄H₈O) (2.8 g, 1.69 mmol) in THF (150 mL). The reaction mixture was stirred at room temperature overnight, then was evaporated to dryness and the solid residue triturated with *n*-hexane (100 mL) to give a brown solid which was collected and dried in vacuo (1.73 g, 76 %). ¹H NMR (400 MHz, [D₅]pyridine, 15 °C, TMS): δ = 6.54 (s, 16H; C₄H₂N), 3.66 (s, 2H; CH), 3.48 (s, 16H; DME), 3.25 (s, 24H; DME), 1.90 (s, 24H; CH₃), 1.46 (s, 24H; CH₃); elemental analysis calcd (%) for 8·4(C₄H₁₀O₂), C₇₆H₁₀₆N₈Na₄O₈Ru₂: C 58.75, H 6.88, N 7.21; found: C 58.73, H 6.21, N 7.09.

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direct methods and refined using the full-matrix least-squares on F^2 with all non-H atoms anisotropically defined (except the external sodium atom and the solvent molecules). For 4426 observed reflections ($I > 2\sigma(I)$) and 921 parameters, the conventional R is 0.0879 ($wR2 = 0.2670$ for 10835 independent reflections). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-154158 (**4**) and CCDC-154159 (**8**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

A Readily Available and User-Friendly Chiral Catalyst for Efficient Enantioselective Olefin Metathesis**

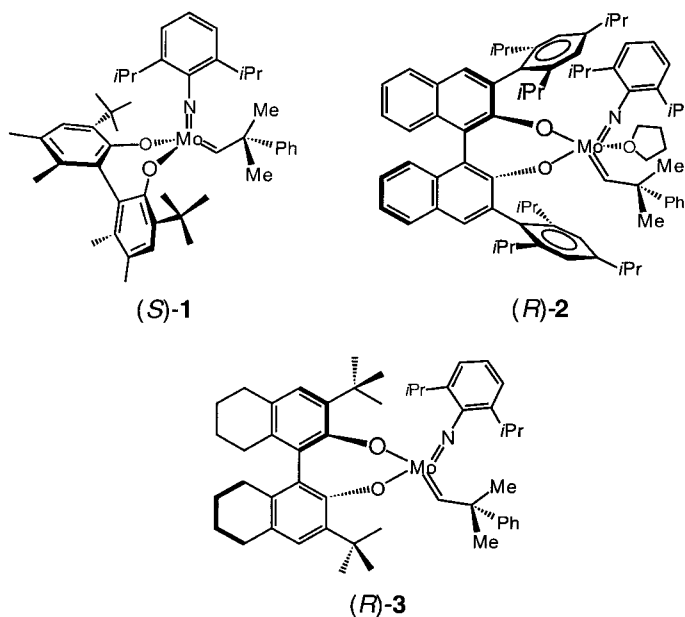
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We recently reported the synthesis and utility of various Mo-based chiral catalysts that promote enantioselective olefin metathesis.^[1] These complexes, represented by (*S*)-**1**^[2] and (*R*)-**2**^[3], are the only existing class of chiral catalysts that efficiently and selectively promote the formation of optically pure or enriched carbo- and heterocycles through asymmetric ring-closing^[4] and ring-opening metathesis (ARCM and AROM, respectively).^[5] One notable difference between **1** and **2** is that biphenolate **1** initiates selective ARCM of five-membered rings and binaphtholate **2** is often the catalyst of choice for the enantioselective synthesis of six-membered analogues.^[3]

From a practical point of view, binaphthol-based systems (e.g., **2**) have a significant advantage: the synthesis of the optically pure diolate begins from the inexpensive and commercially available (*R*)- or (*S*)-binaphthol.^[6] In contrast, access to the optically pure biphenol ligand in **1** and its derivatives requires resolution of the racemic samples by

fractional crystallization of the derived phosphorus(v) mentholates.^[2] We therefore judged that a chiral Mo complex that bears a “biphenol-type” ligand, but is synthesized from the readily available optically pure binaphthol, would be an important and valuable addition to this unique class of chiral catalysts. We also suspected that such a catalyst could exhibit greater generality: its reactivity and selectivity trends may overlap those exhibited by the biphenol- (e.g., **1**) and binaphthol-based complexes (e.g., **2**).

Herein, we report the synthesis, structure, and synthetic utility of chiral complex **3**, a Mo catalyst that resembles a



biphenol-based catalyst (**1**) but, similar to **2**, is easily prepared from optically pure binaphthol. We demonstrate that complex **3** offers a solution to the important problem of practicality in Mo-catalyzed asymmetric olefin metathesis. The new catalyst may be prepared from commercially available starting materials and can be used in situ, without isolation, to effect enantioselective olefin metathesis.

Preparation of chiral catalyst **3** (Scheme 1) begins with catalytic hydrogenation of commercially available, optically pure (*R*)-**4** in the presence of PtO_2 ^[7] under 100 psi (6.9 atm, 690 KPa) H_2 in glacial acetic acid (HOAc).^[8] In a 20 g (69.9 mmol) scale reaction, the desired octahydrobinaphthol **5** is formed in > 98 % yield (cream-colored powder).^[9] Installation of *t*Bu groups at the C2 and C2' sites is carried out by acid-catalyzed alkylation with isobutylene, a procedure that involves the difficult separation of the desired functionalized binaphthol from adventitious oligoisobutylenes; pure dialkylated product is obtained after chromatography on silica gel in 40 % yield. However, when the unpurified mixture is directly treated with 2 equivalents of KH, the derived dipotassium salt (*R*)-**6** is isolated in 85 % yield. Through this procedure, oligoisobutylene impurities are removed by washing with pentane. The resulting dipotassium salt (*R*)-**6** (soon to be commercially available through Strem) does not need further purification before it is employed in the synthesis of **3**.^[10]

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