Synthesis of 4'-Functionalized 2,2':6',2''-Terpyridines via the Pyridone Route: Symmetric and Asymmetric Bis-Complex Formation

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Abstract: 2,2':6',2''-Terpyridines functionalized in the 4'-position have been prepared by reaction of 2,6-bis-(pyrid-2-yl)-4-pyridone under basic conditions with different electrophiles. The electrophiles consist of functionalized alkyl chains, which are terminated with different anionic leaving groups such as bromides, chlorides and tosylates. These reactions yielded terpyridines, which were modified at the 4'-position with heptoxy-, bromodecanoxy-, cyano-propoxy-, allyloxy-, styrene-4-ethoxy-, as well as (methoxy-ethoxy)-ethoxy functionalities. In an approach towards new functional materials based on polymerizable bis-terpyridyl metal-ion complexes, the 4'-epoxy-methoxy terpyridine was complexed with Co(II) in order to yield the paramagnetic bis-complex, which still could be characterized via 1H NMR spectrometry. Additionally, in order to obtain an asymmetric bis-complex with two different terpyridine ligands, methyl-diethyleneoxy-terpyridine-Ru(II)-terpyridine-oxyheptane was prepared utilizing a directed coupling method via Ru(III)/Ru(II) chemistry.

Key words: terpyridines, metal complexes, epoxides, ruthenium, supramolecular chemistry

2,2':6',2''-Terpyridines with a chemical functionality at the 4'-position have been applied in fields such as metallo-supramolecular chemistry, where the metal centers are used to control self organization processes or metal-polymer chemistry, where telechelic terpyridine-functionalized polymeric or non-polymeric building blocks are extended to long chains or networks via metal complexation. Metal-ions suitable for the build-up of such metallo-polymers are transition metals such as Fe(II), Co(II), Ru(II) or Ni(II), which lead to octahedral bis-terpyridyl complexes with high stability constants. In this context, the well-known directed coupling method utilizing Ru(III)/Ru(II) chemistry is of special interest. Ligand A is first complexed with Ru(III) in order to form a monoterpyridine complex and subsequently free terpyridine containing ligand B is added under reductive conditions in order to form A-terpyridine-Ru(II)-terpyridine-B structures. Other applications, in particular concerning 2,2':6',2''-terpyridines with a synthetic handle in the 4'-position lie in the fields of metallo-dendrimers, surface science and biochemistry. Utilizing terpyridines with functionality in the 4'-position as building block offers the advantage of creating linear systems in which the octahedral metal complex is located in the backbone of the metallo-polymer. Also no additional diastereomeric metal complex centers are added because of a terpyridine having C2v symmetry with a rotation axis through the 4'-position, thus leading to no fac or mer (bis-terpyridine) diastereomers upon complexation of 4'-functionalized terpyridines.

For functionalization in the 4'-position mainly two intermediates have been used up to now: 4'-chloro-2,2':6',2''-terpyridine and its precursor 2,6-bis-(pyrid-2-yl)-4-pyridone. Surprisingly, for the latter one there are only few examples reported. In contrast, there are numerous examples utilizing the nucleophilic aromatic substitution of the chloride-function in the 4'-chloro-2,2':6',2''-terpyridine, leading, e.g. to 4'-R-alkoxy-2,2':6',2''-terpyridines. The direct synthesis of 4'-functionalized 2,2':6',2''-terpyridines is also possible via the ‘Kröhnke-method’ for which suitable precursors would have to be designed first. We describe here the synthesis of several new ligands by direct functionalization of the 2,6-bis-(pyrid-2-yl)-4-pyridone. Among the reported functionalities attached to the terpyridine are an epoxide, terminal double bonds, a nitride, a 10-bromodecyloxy as well as a heptoxy and a (methoxyethoxy)-ethoxy chain. As an example for a symmetric terpyridine complex, we chose to react the epoxide-terpyridine with Co(II)-acetate. Co(II) can be reduced to lower oxidation states, which preferentially form mono-terpyridine complexes. Therefore cobalt could be a metal ion suitable for reversible metallo-supramolecular structures. An asymmetric complex was also prepared with 4'-heptoxy-terpyridine and the 4'-(methoxyethoxy)ethoxy-terpyridine utilizing Ru(III)/Ru(II) chemistry. This example shows the feasibility of the synthesis as well as the characterization of a complex combining two different ligands.

As already reported in literature, the alcaloholate of the tautomeric form of the 2,6-bis-(pyrid-2-yl)-4-pyridone 1, 4'-hydroxy-terpyridine, can be prepared in situ in a K2CO3–basic DMF suspension and acts as nucleophile for Sn2 type nucleophilic substitutions. For a nucleophilic attack onto alkyl chains good anionic leaving groups such as halides or tosylates are required. Apart from the (methoxyethoxy)-ethyl-tosylate, which was prepared following standard procedures, all functionalized starting materials...
(bromides and chlorides) were commercially available (Scheme 1).

For obtaining the bromo-decyloxy functionalized terpyridine 2, a 10-fold excess of the bis-functionalized starting material had to be used in order to minimize disubstitution. After precipitation in a 10-fold excess of water, purification including column chromatography and crystallization was necessary for the separation from the bis-terpyridyl by-product. The other functional terpyridines (3–5) were easily prepared in high yields starting from the alkyl bromides through extraction after pouring the reaction mixture into a 10-fold excess of water and subsequent column chromatography. The same general strategy was applied for the products 6 and 7, obtained by chloride substitution. In the case of the epoxy-methoxy-terpyridine 6 special measures had to be taken for purification. Utilizing standard column chromatography on alox N with CHCl₃–MeOH (99:1) as eluent resulted in a quantitative ring opening by nucleophilic attack of MeOH. However, filtration on alox N with anhydrous CHCl₃ as eluent, followed by careful crystallization from THF yielded the pure product. In the cases where the functional groups consisted of double bonds (4 and 7) and the epoxide (6), the reaction temperature was kept below 50 °C in order to avoid by-product formation or degradation. It should be mentioned that the introduction of such sensitive groups as bromides, double bonds or epoxides has not been feasible for the functionalization route via the 4’-chloro-2,2’6’,2”-terpyridine. Apart from the availability of nucleophilic starting material in the latter case, this also has to do with the stronger basic system KOH–DMSO, which is required for the nucleophilic aromatic substitution compared to K₂CO₃–DMF used for the S₂N₂-type reaction here. The (methoxyethoxy)-ethoxy-terpyridine 8, which was prepared by the reaction of 1 with (methoxyethoxy)-ethyl-tosylate, was obtained according to the synthesis of the compounds 3–5 utilizing the alkyl bromides as starting material. All of the compounds reported here were synthesized in acceptable yields between 60–92%. The reason for the rather low yields in the case of the bromo-decyloxy functionalized terpyridine 2 and the epoxy-methoxy-terpyridine 6 can be found in the extensive work-up procedures.

The symmetric complex 9 was formed by the reaction of two equivalents of epoxy-methoxy-terpyridine 6 with one equivalent of Co(II)acetate (Scheme 2).

Because of the vulnerability of the epoxide group to MeOH, the reaction was carried out stirring at room temperature for 30 minutes. The addition of excess NH₄PF₆ resulted in immediate quantitative precipitation of the complex.

Scheme 1 Functionalization reactions of 2,6-bis(pyrid-2-yl)-4-pyridone (in K₂CO₃–DMF).

Scheme 2 Synthesis of the symmetric bis(epoxide-terpyridine)-Co(II) complex 9.
crude product. After filtration and washing with MeOH and water the pure complex was obtained. The shifts in the $^1$H NMR are influenced by the paramagnetism of Co(II) (Figure 1). Due to the hyperfine interaction of the unpaired Co(II) electrons with the ligand protons a shift to low field is observed with the signals still being sharp enough for integration.$^{16}$ Through comparison with similar complexes reported by Constable et al. the spin-state of the Co(II) can be assigned as low-spin.$^{17}$

The existence of the complex 9 was proven by MALDI–TOF mass spectrometry. Figure 2 shows the spectrum obtained for the bis(epoxide-terpyridine)-Co(II) complex 9, recorded with the matrix DHB (dihydroxy benzoic acid). The spectrum shows four isotope distributions which could all be assigned. All fragments refer to singly positive charged compounds. The peaks at $m/z$ 814 and 669 represent the complex without one and none counter-ions, respectively. These fragment types are often observed for bis-terpyridyl complexes.$^{18}$ The fragment at $m/z$ 517 refers to the complex without the counter-ions and without one ligand plus matrix minus a proton. At $m/z$ 1033 the dimer of the latter fragment minus one proton is detected as can be shown through comparison with the simulated spectrum.

For the synthesis of the asymmetric complex with two different ligands the heptoxy functionalized terpyridine was first reacted with Ru(III) chloride in order to yield the heptoxy-terpyridine-Ru(III) mono complex 10. After washing with MeOH and Et$_2$O, followed by drying in vacuo, the compound was then used without further purification in order to form the asymmetric complex 11 with the monomethyl-diethyleneglycol-terpyridine (Scheme 3).

The reaction was carried out in EtOH with N-ethyl morpholine as catalyst wherein the EtOH is the reducing agent. After stirring for 4 hours at reflux the complex was precipitated with an excess of 40 equivalents of NH$_4$PF$_6$. Recrystallization by slow diffusion of Et$_2$O into a solution of the crude complex in CH$_3$CN yielded the pure product as red crystals. Apart from characterization including $^1$H-,$^{13}$C NMR, MALDI–TOF mass spectrometry and elemental analysis, 2-dimensional $^1$H–$^1$H-COSY NMR was used.

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Figure 1 $^1$H NMR of the Co(II)-complex 9 (in CD$_3$CN).

Figure 2 MALDI–TOF–MS of bis(epoxide-terpyridine)Co(II) complex 8.

Scheme 3 Asymmetric bis-complex formation via Ru(III)/Ru(II) chemistry.

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for the characterization of the asymmetric bis-complex 11 (Figure 3).

Figure 3 1H–1H-COSY-NMR of the asymmetric complex 11 (in CD3CN).

In the terpyridine region, all signals could be assigned via the cross-peaks (Figure 3, inset). It could be shown that the two peaks at 8.28 and 8.33 ppm are actually two singlets for the 3',5'-protons of the two different terpyridine ligands. Furthermore, the CH2 signals of the (methoxy-ethoxy)-ethoxy and the CH2O signal of the hexeyl-rest could be distinguished. Also all aliphatic methylene groups were assigned properly.

The new 4'-functionalized terpyridine ligands described here were synthesized in good yields starting from 2,6-bis(pyrid-2-yl)-4-pyridone. The epoxide-terpyridine was suitable for the synthesis of the symmetrical complex with Co(II), which could be characterized sufficiently by standard techniques and also by NMR. Additionally, an asymmetric bis(terpyridine) containing different functionalities was prepared, utilizing the well-known Ru(III)/Ru(II) chemistry and was characterized with standard techniques and also by 2-dimensional NMR. This complex represents a model for the combination of different non-polymeric functionalities (hydrophobic/hydrophilic), which could be important for the design of new metallo-block-copolymers.

Analyses were carried out on a Perkin Elmer Series II 2400. Melting points were obtained from a Büchi Melting Point B-540. 

4-(10-Bromo-decyloxy)-2,2':6',2''-terpyridine (2)

To a stirred suspension of powdered KOH (680 mg, 12.1 mmol) in DMF (100 mL) 2,6-bis(pyrid-2-yl)-4-pyridone (I) (1.00 g, 4.01 mmol) was added at r.t. After 20 min 1,10-dibromodecane (7.63 g, 25.4 mmol) was added, the mixture was stirred for 90 min and then poured into deionised water (600 mL). The aq phase was removed by filtration, the product was washed with deionised water and then precipitated in n-pentane (50 mL). The crude white product was purified by column chromatography (alox, eluent CH2Cl2) and recrystallized from EtOH yielding 1.13 g (60%) of a white crystalline material; Rf 0.76 (alox, CH2Cl2); mp 104 °C.

1H NMR (300 MHz, CDCl3): δ = 1.31–1.58 (m, 12 H, H-alkyl), 1.80–2.00 (m, 4 H, H5, H6), 2.31 (t, J = 6.59, 3 H, H3), 4.22 (t, J = 6.59 Hz, 2 H, H3), 7.32 (ddd, J = 7.5, J = 4.8, J = 1.2 Hz, 2 H, H5,6), 7.84 (ddd, J = 8.0, J = 7.5, J = 1.8 Hz, 2 H, H5,6), 8.01 (s, 2 H, H1,5), 8.62 (ddd, J = 8.0, J = 1.0, J = 1.0 Hz, 2 H, H1,5), 8.69 (ddd, J = 4.7, J = 1.8, J = 0.9 Hz, 2 H, H1,5).

13C NMR (75 MHz, CDCl3): δ = 25.9 (C6), 28.2 (C7), 28.7 (C8), 29.0 (C9), 29.2 (C10), 29.4 (C11), 32.8 (C12), 34.0 (C13), 68.2 (C14), 107.4 (C15), 121.3 (C16), 123.7 (C17), 136.8 (C18, C19), 149.0 (C20), 156.2 (C21), 157.0 (C22), 167.3 (C23).

MS (MALDI–TOF, matrix: dithranol): m/z = 468 [M + H]+.

Anal. Calcd for C25H30BrN3O (468.43): C, 64.10; H, 6.46; N, 8.97. Found: C, 63.87; H, 6.06; N, 8.93.

4-Heptyloxy-2,2':6',2''-terpyridine (3)

K2CO3 (3.5 g, 25.4 mmol) was added, the mixture was stirred for 90 min and then added dropwise to the mixture and stirring was continued overnight. The resulting mixture was poured into water and extracted with 3 × 25 mL CHCl3. After drying the organic layer with Na2SO4 the product was purified by column chromatography (alox, CH2Cl2) to yield 3.0 g (68%) of compound 3; mp 64 °C.

IR (ATR): 2941, 2920, 2867, 2853 (C–C), 1597, 1580, 1562 (C=C, CH=N, terpyridine) cm–1.

Anal. Calcd for C25H30BrN3O (468.43): C, 64.10; H, 6.46; N, 8.97. Found: C, 63.87; H, 6.06; N, 8.93.

4-Allyloxy-2,2':6',2''-terpyridine (4)

To a solution of I (2.5 g, 10.0 mmol) and K2CO3 (4.2 g, 30 mmol) in anhyd DMF (20 mL) a solution of allyl bromide (1.15 g, 9.50 mmol) in anhyd DMF (10 mL) was added dropwise at 50 °C. Stirring was continued overnight, after which the reaction mixture was poured into deionised water (70 mL) and extracted with CH2Cl2 (3 × 50 mL). The combined organic layers were dried over Na2SO4, filtered and evaporated in vacuo. The crude product was purified by column chromatography (alox, eluent CH2Cl2) and recrystallized from EtOH yielding 1.13 g (60%) of a white crystalline material; Rf 0.76 (alox, CH2Cl2); mp 104 °C.

1H NMR (400 MHz, CDCl3): δ = 0.90 (t, J = 6.59, 3 H, H3), 1.28–1.44 (m, 6 H, H-alkyl), 1.46–1.54 (m, 2 H, H-alkyl), 1.81–1.89 (m, 2 H, H-alkyl), 2.6 (t, J = 6.59 Hz, 2 H, H3), 7.32 (ddd, J = 8.1, J = 5.1, J = 1.5 Hz, 2 H, H5,6), 7.84 (ddd, J = 8.1, J = 8.1, J = 1.5 Hz, 2 H, H5,6), 8.01 (s, 2 H, H5,6), 8.62 (dd, J = 8.1, J = 1.5 Hz, 2 H, H1,5), 8.69 (d, J = 5.9 Hz, 2 H, H1,5).

13C NMR (100 MHz, CDCl3): δ = 14.1 (C1), 22.6, 25.9, 29.0, 29.7, 31.8 (C-alkyl), 68.2 (C7), 107.4 (C12), 121.3 (C13), 123.7 (C17), 136.7 (C18), 149.0 (C20), 156.2 (C21), 157.0 (C22), 167.3 (C23).

UV–Vis (CH3CN): λmax (ε, M–1 cm–1) = 277 (25300), 240.1 (27900) nm.

MS (MALDI–TOF, matrix: dithranol): m/z = 348 [M + H]+.


Chemicals were obtained from Sigma-Aldrich. 2,6-Bis-(pyrid-2-yl)-4-pyridone was synthesized according to ref.1b 1H and 13C NMR were recorded on a Varian Mercury 400 spectrometer and the chemical shifts were calibrated to the solvent peaks. For more clarity, the carbons and hydrogens of the alkyl spacers are numbered using Greek symbols starting from the first carbon at the functionality and ending at the carbon next to the 4'-ether function at the terpyridine. UV–Vis spectra were recorded on a Perkin Elmer Lambda-45 (using 1 cm cuvettes) and IR spectra were recorded on a Perkin Elmer Spectrum One. MALDI–TOF mass spectra were recorded on a Perseptive Biosystems Voyager-DE STR Biospectrometry and EIMS were obtained from a Shimadzu GCMS-QP5000.
chromatography (alox N, CH₂Cl₂), yielding 2.52 g (92%) of 4 as a white solid; mp 103 °C.

IR (ATR): 3091, 3051, 3011 (CH), 2913, 2862 (CH₂), 1600, 1584, 1563 (C=C, C=N, terpyridine) cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 6.63–6.88 (m, 2 H, H₅), 5.43–5.61 (m, 1 H, H₄), 6.00–6.18 (m, 1 H, H₆), 7.30 (ddd, 3J = 7.5, 4.8, 2.8 Hz, 2 H, H₃), 7.81 (ddd, 3J = 8.0, 7.5, 1.8 Hz, 2 H, H₄), 8.04 (2 × s, 2 H, H₅), 8.60 (dt, 3J = 8.0, 1.0 Hz, 1 H, H₆), 8.67 (dd, 3J = 4.8, 1.8 Hz, 1 H, H₈).

UV–Vis (CH₃CN): 3070, 2931, 2804 (CH₃, CH₂); 1599, 1582, 1564 (C=C, C=N, terpyridine) cm⁻¹.

IR (ATR): 3088, 3052, 2925 (CH, CH₂), 1683 (C=C styrane), 1600, 1582, 1561 (C=C, C=N, terpyridine) cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 2.11–2.28 (m, 2 H, H₅), 2.61 (t, 3J = 6.8 Hz, 2 H, H₆), 4.32 (t, 3J = 6.0 Hz, 2 H, H₇), 7.28 (ddd, 3J = 7.5, 4.8, 1.2 Hz, 2 H, H₄), 7.81 (ddd, 3J = 8.0, 7.5, 1.8 Hz, 2 H, H₆), 8.11 (s, 2 H, H₃), 8.58 (ddd, 3J = 8.0, 7.5, 1.0 Hz, 2 H, H₄), 8.67 (ddd, 3J = 4.8, 1.8, 1.0 Hz, 2 H, H₆).

MS (MALDI-TOF, matrix: dithranol): m/z = 306 [M + H⁺].

UV–Vis (CH₃CN): λ_max (ε, M⁻¹cm⁻¹) = 275 (25000), 241 (27100) nm.


Found: C, 78.70; H, 5.19; N, 11.37.

4-(3-Vinylbenzeneoxy)-2,2',6',2''-terpyridines via the Pyridone Route

To a solution of 1 (349 mg, 1.80 mmol) and K₂CO₃ (756 mg, 5.40 mmol) in anhyd DMF (25 mL) a solution of 4-vinylbenzenechloride (90% pure) (250 mg, 1.64 mmol) in anhyd DMF (10 mL) was added dropwise at 50 °C. Stirring was continued overnight, after which the reaction mixture was poured into deionised water (100 mL) and extracted with CH₂Cl₂ (3 × 50 mL). The combined organic layers were dried over Na₂SO₄, filtered and evaporated in vacuo. The crude product was purified by column chromatography (alox N, CH₂Cl₂) yielding 380 mg of an off-white solid; mp 124 °C.

IR (ATR): 3088, 3052, 2925 (CH, CH₂), 1683 (C=C styrane), 1600, 1582, 1561 (C=C, C=N, terpyridine) cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 5.23 (dd, 3J = 7.2, 0.9 Hz, 1 H, H₁), 5.26 (s, 2 H, OCH₃), 5.75 (dd, 3J = 17.6, 0.9 Hz, 1 H, H₁), 6.72 (ddd, 3J = 17.6, 7.2, 0.9 Hz, 1 H, H₂), 7.28 (ddd, 3J = 7.5, 4.8, 1.2 Hz, 2 H, H₃), 7.40–7.43 (m, 4 H, H aryl).

MS (MALDI-TOF, matrix: dithranol): m/z = 365 (100) [M⁺].

UV–Vis (CH₃CN): λ_max (ε, M⁻¹cm⁻¹) = 275 (27100), 241 (41900) nm.


Found: C, 78.56; H, 5.39; N, 11.37.

4-[(1-Methoxyethoxy)ethoxy]-2,2',6',2''-terpyridine (8)

To a solution of 1 (3.55 g, 14.2 mmol) and K₂CO₃ (5.96 g, 42.5 mmol) in anhyd DMF (100 mL) a solution of 2-(1-methoxyethoxy)ethoxy-tosylate (3.55 g, 12.8 mmol) in anhyd DMF (50 mL) at 80 °C. Stirring was continued overnight, after which the reaction mixture was poured into deionised water (250 mL) and extracted with CH₂Cl₂ (3 × 150 mL). The combined organic layers were dried over Na₂SO₄, filtered and evaporated in vacuo. The crude product was purified by column chromatography (alox N, CH₂Cl₂) yielding 3.40 g (77%) of 8 as a white solid; m.p. 63 °C.

IR (ATR): 3100, 2910, 2804 (CH₃, CH₂), 1599, 1582, 1564 (C=C, C=N, terpyridine) cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 3.40 (s, 3 H, H₂), 3.58 (t, 3J = 4.4 Hz, 2 H, H₃), 3.75 (t, 3J = 4.0 Hz, 2 H, H₄), 4.41 (t, 3J = 4.8 Hz, 2 H, H₅), 7.31 (dd, 3J = 7.5, 4.8 Hz, 1.8 Hz, 2 H, H₆), 7.84 (dd, 3J = 8.0, 7.5, 1.8 Hz, 2 H, H₇), 8.04 (s, 2 H, H₈), 8.60 (dt, 3J = 8.0, 1.0 Hz, 1 H, H₉), 8.67 (dt, 3J = 4.8, 1.8 Hz, 1 H, H₈).

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mixed with of RuCl₃·H₂O (210 mg, 1.01 mmol) and EtOH. The sus-

1H NMR (400 MHz, CDCl₃): δ = 59.0 (C₆), 67.7 (C₅), 69.4 (C₄),
70.8 (C₁), 71.9 (C₁), 107.4 (C₆), 121.2 (C₁), 123.7 (C₉), 136.7
(C₁₀), 149.0 (C₁₀), 156.0 (C₉), 157.4 (C₈), 166.9 (C₇).

MS (EI): m/z (% = 350) [M⁺].

UV/Vis (CH₃CN): λmax (c, M⁻¹·cm⁻¹) = 277 (24900), 240 (26900)
nm.

Anal. Calcd for C₉H₃₂N₂O₂ (351.41): C, 68.36; H, 6.02; N, 11.96.

MS (MALDI–TOF, matrix: dithranol): m/z = 517 [M – ligand – 2 PF₆⁻].

71.32, 72.59 [C-ethoxy(8)], 111.81, 111.93, 125.17, 125.20,
128.25, 128.29, 138.57, 153.40, 157.39, 159.18, 166.98, 166.72 (all
terpyridine).

MS (MALDI-TOF, matrix: dithanol): m/z = 800.09 [M – 2 PF₆⁻].

MS (ESI): m/z = 399.2 (M – 2 PF₆⁻), 494.6 (M – PF₆⁻).

UV–Vis (CH₃CN): λmax (c, M⁻¹·cm⁻¹) = 238.5 (67100), 264.4
(66200), 302.0 (74600), 486.0 (22900) nm.

Anal. Calcd for C₉H₉₂N₂O₄RuP₂F₁₂ (1089.86): C, 46.29; H, 4.25;
N, 8.76. Found: C, 44.76; H, 3.16; N, 8.59.

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