

Diazadiene Ligands

C–C Coupling and C–H Bond Activation—Unexpected Pathways in the Reactions of $[\text{Yb}(\eta^5\text{-C}_{13}\text{H}_9)_2(\text{thf})_2]$ with Diazadienes**

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The diversity of the coordination and redox properties of 1,4-disubstituted diazadienes (DAD) makes them advantageous ligands for transition-metal chemistry. The DAD molecule can coordinate to a metal atom as a neutral ligand. Possessing a quite pronounced electron affinity^[1] it can oxidize electro-positive lanthanide metals by accepting one or two electrons to form the radical anion^[2] or dianion,^[3] respectively. Owing to the low energy of the π^* orbital of the DAD ligands,^[1c] their complexes with ytterbium, which forms two stable

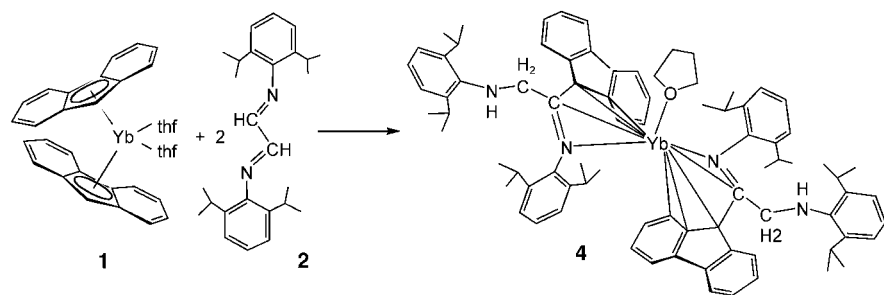
oxidation states and is characterized by a low potential of the $\text{Yb}^{\text{II}}/\text{Yb}^{\text{III}}$ transformation,^[4] are of particular interest as promising objects for investigating intramolecular metal–ligand electron transfer. In our previous studies the variable-temperature investigation of the magnetic properties of the complex $[(t\text{BuNCHCHN}t\text{Bu})_3\text{Yb}]^{[2b]}$ suggested to us the existence of temperature-induced valence tautomerism for this compound. Recently, for the complexes $[\text{YbR}_2(t\text{-BuNCHCHN}t\text{Bu})]$ ($\text{R} = \text{Cp} = \text{C}_5\text{H}_5$ or $\text{R} = \text{Cp}^* = \text{C}_5\text{Me}_5$) we demonstrated that the steric repulsion of DAD and Cp ligands as a result of their bulk might serve as a tool for tuning the Yb–N bond lengths and eventually determine the reversibility of the Yb–DAD electron transfer.^[2f,g] As part of our continuing studies on intramolecular redox processes in ytterbium complexes with redox-active ligands we attempted to synthesize novel mixed-ligand compounds with sterically demanding diazadienes. Herein we report the unexpected reactivity of $[\text{Yb}(\text{C}_{13}\text{H}_9)_2(\text{thf})_2]$ (**1**)^[5] towards diazadienes $[(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{-N}=\text{CR}=\text{CR}=\text{N}-(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)]$ ($\text{R} = \text{H}$ (**2**), Me (**3**)) which results either in the coupling of the fluorenyl and DAD fragments or in proton abstraction from the DAD molecule, depending on the substituent R on the carbon atom of the imino group.

$t\text{BuN}=\text{CH}-\text{CH}=\text{N}t\text{Bu}$ readily oxidizes ytterbocenes $[\text{YbR}_2(\text{thf})_2]$ ($\text{R} = \text{Cp}, \text{Cp}^*$) to afford the trivalent ytterbium derivatives $[\text{YbR}_2(t\text{BuNCHCHN}t\text{Bu})]^{[2f,g]}$ which contain a DAD radical anion. Unexpectedly, the reactions of the bisfluorenyl analogue **1** with bulky diazadienes **2** and **3** under the same conditions do not lead to oxidation of the ytterbium atom but result in the formation of the Yb^{II} derivatives. Thus, the reaction of **1** with a twofold molar excess of **2** led to the isolation of the unexpected product $[\text{Yb}\{\eta^5\text{-C}_{13}\text{H}_8\text{C}(\text{=N}[2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3])\text{CH}_2\text{NHC}_6\text{H}_3(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\}_2(\text{thf})]$ (**4**) in 80 % yield (Scheme 1).

Complex **4** is readily soluble in ethers and toluene, but sparingly soluble in hexane. The diamagnetic properties of **4** corroborate the divalent state of ytterbium.^[6] Crystallization of **4** by slow cooling of the solution in hexane resulted in single crystals of the hexane solvate **4**· C_6H_{14} that were suitable for crystal-structure analysis (Figure 1). The X-ray diffraction study revealed that the Yb^{II} cation is η^5 -coordinated by two novel multifunctional ligands $\{\text{C}_{13}\text{H}_8\text{C}(\text{=N}[2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3])\text{CH}_2\text{NHC}_6\text{H}_3(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\}^-$, which arise from unprecedented coupling of the allylic carbon atom of the fluorenyl ligand with the imino carbon atom of the diazadiene **2**. The C–C bond (1.426(3), 1.434(3) Å) formation in **4** also implies that the two H atoms initially bonded to the coupled carbon atoms migrate to the second imino group, resulting in the hydrogenated $\text{CH}_2\text{-NH}$ fragment. Unlike the η^5 -bonding of the fluorenyl fragment to the Yb atom in the starting complex **1**,^[5] a rather unusual η^3 -type of coordination through one carbon atom of the five-membered ring and two carbon atoms of the six-membered ring occurs in **4**. The η^2 -coordination of the imino group to the Yb atom results in the formation of the planar (deviation from the plane is 0.11 Å) η^5 -bonded heteropentadienyl frame. The C–C bond lengths within this frame (1.398(3)–1.461(3) Å) fall within the range of values for aromatic C–C bonds,^[7] and the C–N bond lengths (1.324(3), 1.319(3) Å) are slightly longer than the

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Scheme 1. Reaction of **1** and **2** to give **4**. Reagents and conditions: **1**, **2** (2 equiv), THF, 60 °C, 30 min; then toluene, 60 °C, 1 h; then toluene, 60 °C, 2 h.

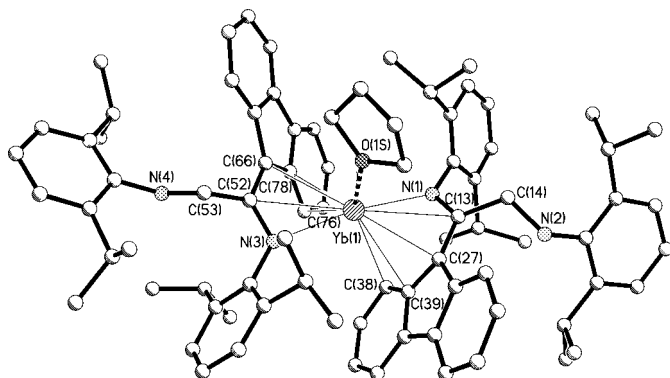


Figure 1. ORTEP representation of structure **4**. Selected bond lengths [Å] and angles [°]: Yb(1)–N(3) 2.445(2), Yb(1)–N(1) 2.466(2), Yb(1)–C(78) 2.759(2), Yb(1)–C(39) 2.768(2), Yb(1)–C(77) 2.786(2), Yb(1)–C(27) 2.795(2), Yb(1)–C(38) 2.798(2), Yb(1)–C(66) 2.868(2), Yb(1)–C(13) 2.933(2), Yb(1)–C(52) 2.952(2), N(1)–C(13) 1.324(3), N(1)–C(1) 1.443(3), C(13)–C(27) 1.426(3), C(13)–C(14) 1.521(3), C(27)–C(39) 1.459(3), C(38)–C(39) 1.398(3), N(2)–C(14) 1.447(3), N(3)–C(52) 1.319(3), N(4)–C(53) 1.464(3), C(52)–C(53) 1.514(3), C(52)–C(66) 1.434(3), C(66)–C(78) 1.461(3), C(77)–C(78) 1.403(3); N(3)–Yb(1)–C(77) 70.80(6), N(1)–Yb(1)–C(38) 70.21(6), O(1S)–Yb(1)–N(3) 97.56(5), O(1S)–Yb(1)–N(1) 96.31(5).

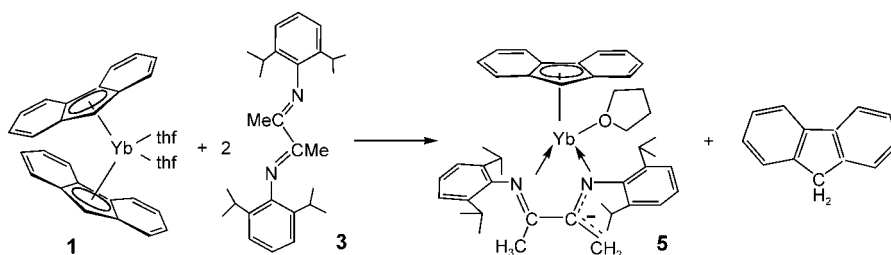
C=N bond in the parent diazadiene (1.266(3) Å).^[8] Such a bonding situation is evidence for a delocalized π system in the heteropentadienyl fragment. The dihedral angle between the N(3)–C(52)–C(66)–C(78)–C(77) and the N(1)–C(13)–C(27)–C(39)–C(38) planes is 64.4° and the angle Ct–Yb–Ct (Ct are the centroids of the N(3)–C(52)–C(66)–C(78)–C(77) and the N(1)–C(13)–C(27)–C(39)–C(38) rings) is 147.2° (reference: 136.3(3)° in [YbCp*₂(C₅H₅N)₂]).^[9] The Yb–C bond lengths in **4** (2.759(2)–2.952(2) Å) are somewhat longer than those in the starting complex **1** and are comparable to the distances reported for the Yb^{II}–bispentadienyl derivative [Yb{4,4'-(CH₂)₂-(2-C₆H₃)₂}(thf)₂] (2.709(9)–2.909(9) Å).^[10] The Yb–N bond lengths are very similar to those in Yb^{II}– β -diketiminates (2.418(9)–2.423(9) Å).^[11] The arrangement around the ytterbium atom in **4** determines the geometry of the hetero-

pentadienyl bent sandwich complex. Spectroscopic data consistent with this formulation were also obtained.

In an attempt to obtain insight into the mechanism of the observed ligand transformation, we investigated the reaction of **1** with the diazadiene **3** under the same conditions. We found that replacement of the imino hydrogen atoms by two methyl groups dramatically influences the reaction pathway and leads to the formation of different products. We followed the procedure described above and isolated the novel Yb^{II} derivative **5** (64%) and fluorene (81%). (Scheme 2)

Complex **5** was isolated as a deep green crystalline solid that is readily soluble in toluene but sparingly soluble in hexane. The compound is diamagnetic, which corresponds to the Yb^{II} oxidation state. Single crystals suitable for X-ray crystal-structure analysis (Figure 2) were obtained by recrystallization of **5** from toluene/hexane mixtures.

The crystal-structure analysis showed that the ytterbium atom in **5** is η^5 -coordinated by the sole fluorenyl ligand and by the two nitrogen atoms of the novel monoanionic ligand [(2,6-*i*Pr₂C₆H₃)N=C(CH₃)–C(CH₂)=N(2,6-*i*Pr₂C₆H₃)][–] (**6**), which results from proton abstraction from the methyl substituent of the imino group of **3**. The Yb–C bond lengths in **5** are in the range 2.655(2)–2.770(3) Å, slightly shorter than those in **1**. The Yb–N bonds in **5** are non-equivalent. The Yb(1)–N(2) bond length (2.315(2) Å) is similar to that of the Yb^{II}–N covalent bond in the complex [Yb{N(SiMe₃)}(thf)BPh₄] (2.314(2) Å)^[12a] and slightly longer than that in the complex [Yb{N(SiMe₃)₂}(Me₂P(CH₂)₂PMe₂)] (2.329(2) Å).^[12b] The Yb(1)–N(1) bond is essentially longer (2.388(2) Å), but nevertheless much shorter than the Yb^{II}–N coordination bonds (2.58(1)–2.65(1)).^[9,13] The N=C bonds of the NCCN fragment in **5** are longer than the corresponding bonds of the



Scheme 2. Reaction of **1** and **3** to give **5** and fluorene. Reagents and conditions: **1**, **3** (2 equiv), THF, 60 °C, 30 min; then toluene, 60 °C, 1 h; then toluene, 60 °C, 2 h.

parent diazadiene **3** (1.279(3), 1.280(3) Å)^[14] and differ significantly as well: N(1)–C(26) 1.318(3) Å and N(2)–C(28) 1.353(3) Å. The C–C bond length of the diazadiene fragment in **5** remains similar to that in **3** (1.498(3) Å).^[14] A short C(28)–C(29) bond length (1.398(4) Å) comparable to that of aromatic C–C bonds^[7] together with a flat geometry around the C(29) atom (the sum of the bond angles is 359.8°) provide evidence for sp² hybridization at this carbon atom.

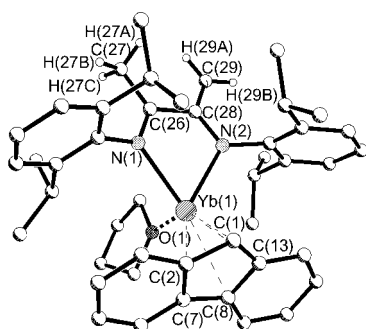


Figure 2. ORTEP representation of structure **5**. Selected bond lengths [Å] and angles [°]: Yb(1)–C(1) 2.649(3), Yb(1)–C(2) 2.655(2), Yb(1)–C(7) 2.727(2), Yb(1)–C(13) 2.744(3), Yb(1)–C(8) 2.770(3), Yb(1)–N(2) 2.315(2), Yb(1)–O(1) 2.352(2), Yb(1)–N(1) 2.388(2), N(1)–C(26) 1.318(3), N(1)–C(14) 1.439(3), N(2)–C(28) 1.353(3), N(2)–C(30) 1.435(3), C(26)–C(28) 1.499(4), C(26)–C(27) 1.471(4), C(28)–C(29) 1.398(4); N(2)–Yb(1)–O(1) 99.76(7), N(2)–Yb(1)–N(1) 9.37(7), O(1)–Yb(1)–N(1) 95.65(7), H(29A)–C(29)–H(29B) 119.5(2), C(28)–C(29)–H(29B) 119.3(2), C(28)–C(29)–H(29A) 121.0(2).

Unlike the geometry of the DAD radical anions in Yb^{III} complexes,^[2b,f,g] which exhibit redistribution of the bond distances (characteristic of delocalized NCCN π systems), the geometry of the monoanionic ligand **6** in **5** is indicative of a partial double bonding and delocalization of the negative charge only occurs in the N(2)–C(28)–C(29) fragment (Scheme 3).



Scheme 3. The geometry of the monoanionic ligand **6** is indicative of a partial double bond. Delocalization of the negative charge only occurs in the N(2)–C(28)–C(29) fragment.

The higher value of the effective negative charge on the N(2) atom results in the non-equivalence of the Yb–N bonds and in the shortening of the Yb(1)–N(2) bond. The ¹H and ¹³C NMR spectra of **5** are consistent with the structural data. The protons of the methyl radical by the imino group appear in the ¹H NMR spectrum as a singlet at $\delta = 1.67$ ppm, whereas the two methylene protons become diastereotopic as a result of partial double bonding in the NCC₂H₂ group, giving rise to two singlets of equal intensity at $\delta = 3.94$ and 4.40 ppm.

Isolation of fluorene from the reaction in nearly quantitative yield proves that the fluorenyl anion is responsible for the abstraction of the proton from **3** and for the formation of the ligand **6**. Similar C–H bond activations in the ytterbium amido complexes were previously reported by Deacon and Forsyth^[12a] and by Dehnicke and co-workers.^[15]

Unfortunately, at the present stage of our investigation we are unable to rationalize definitely the formation of the complexes **4** and **5**. Undoubtedly, the first step is coordination of the diazadiene to the ytterbium atom and formation of the mixed-ligand derivatives [(C₁₃H₉)₂Yb(DAD)]. We presume

that oxidation of the ytterbium atom to Yb^{III} occurs in this step and we are currently attempting to prove of this hypothesis. Steric crowding of the coordination sphere of the ytterbium atom is most likely the factor that drives the transformation of the formed species into complexes **4** and **5**. Further work on this subject is being actively pursued at the moment.

Experimental Section

4: A solution of **2** (0.99 g, 2.65 mmol) in THF (10 mL) was added to a solution of **1** (0.86 g, 1.32 mmol) in THF (20 mL) and the reaction mixture was heated at 60 °C for 0.5 h. THF was evaporated in vacuo, toluene (20 mL) was added, and the reaction mixture was stirred at 60 °C for 1 h. The volatile material was evaporated in vacuo, and another portion of toluene (20 mL) was added. The mixture was stirred at 60 °C for an additional 2 h, after which time the solvent was evaporated in vacuo and the deep red solid residue was dissolved in hexane (35 mL). Slow concentration of the solution in hexane at –20 °C resulted in crystals of **4**. The mother liquor was decanted, and the crystals were washed with cold hexane and dried in vacuo at room temperature for 45 min to afford ruby-red crystals of **4** (1.41 g, 80 %). Elemental analysis: calcd (%) for C₈₂H₉₈N₄OYb: C 73.72, H 7.33, Yb 12.95; found: C 73.95, H 7.42, Yb 12.00; ¹H NMR (200 MHz, [D₆]benzene, 20 °C): $\delta = 0.76$ (d, ³J_{HH} = 6.6 Hz, 18H; CH(CH₃)₂), 0.92 (d, ³J_{HH} = 6.6 Hz, 12H; CH(CH₃)₂), 1.05 (d, ³J_{HH} = 6.6 Hz, 12H; CH(CH₃)₂), 1.16 (m, 6H; CH(CH₃)₂), 1.20 (s, 4H; β -CH₂ (thf)), 1.42 (m, 4H; CH(CH₃)₂), 2.47 (sept, ³J_{HH} = 6.8 Hz, 4H; CH(CH₃)₂), 3.33 (br s, 4H; α -CH₂ (thf)), 3.56 (br s, 1H; NH), 4.01 (t, ³J_{HH} = 5.2 Hz, 1H; NH), 4.40 (d, ³J_{HH} = 4.4 Hz, 4H; CH₂), 6.94 (s, 6H; Ar-H), 7.10 (s, 6H; Ar-H), 7.15–7.46 (m, 8H; Ar-H), 7.92 (d, ³J_{HH} = 7.2 Hz, 4H; Ar-H), 8.16 ppm (d, ³J_{HH} = 7.6 Hz, 4H; Ar-H); ¹³C NMR (50 MHz, [D₆]benzene, 20 °C): $\delta = 23.6$, 23.7, 25.0, 25.1 (CH(CH₃)₂), 25.4 (β -CH₂ (thf)), 27.5, 28.6 (CH(CH₃)₂), 52.6 (CH₂NH), 70.2 (α -CH₂ (thf)), 92.7 (Flu-C = NAr), 119.4, 121.5, 122.4, 123.5, 124.4, 125.5, 127.0, 128.1 (CH, Ar-C), 114.9, 131.9, 136.5, 139.8, 140.1, 144.0, 144.8, 172.8 ppm (quat. C, Ar-C); IR (Nujol, KBr): $\tilde{\nu} = 3400$ (w), 3060 (w), 1640 (m), 1580 (m), 1300 (s), 1160 (m), 1080 (m), 950 (m), 860 (m), 780 (s), 750 (s), 730 cm^{–1} (s).

5: A solution of **3** (0.82 g, 2.03 mmol) in THF (10 mL) was added to a solution of **1** (0.65 g, 1.00 mmol) in THF (20 mL) and the reaction mixture was heated at 60 °C for 0.5 h. THF was evaporated in vacuo, toluene (20 mL) was added, and the reaction mixture was stirred at 60 °C for 1 h. The volatile material was evaporated in vacuo, and another portion of toluene (20 mL) was added. The mixture was stirred at 60 °C for an additional 2 h, after which time the solvent was evaporated in vacuo and the deep green solid residue was recrystallized from a mixture of toluene/hexane at –20 °C. The mother liquor was decanted and the crystals were washed with cold hexane dried in vacuo at room temperature for 45 min to afford deep green crystals of **5** (0.53 g, 64 %). The volatile material was removed from the mother liquor in vacuo, and fluorene (0.14 g, 81 %) was sublimed from the solid residue. Elemental analysis: calcd (%) for C₄₅H₅₆N₂OYb: C 66.44, H 6.88, Yb 21.26; found: C 66.64, H 6.70, Yb 21.20; ¹H NMR (200 MHz, [D₆]benzene, 20 °C): $\delta = 1.06$ –1.42 (m, 28H; CH(CH₃)₂ and β -CH₂ (thf)), 1.67 (s, 3H; N = CCH₃), 2.63 (br s, 2H; CH(CH₃)₂), 3.16 (br s, 2H; CH(CH₃)₂), 3.38 (br s, 4H; α -CH₂ (thf)), 3.94 (s, 1H; N = CCHH), 4.40 (s, 1H; N = CCHH), 6.63 (s, 1H; Flu-H), 6.97–7.02 (m, 4H; Ar-H), 7.24–7.42 (m, 8H; Ar-H), 7.99 ppm (m, 2H; Ar-H); ¹³C NMR (50 MHz, [D₆]benzene, 20 °C): $\delta = 19.0$ (N = CCH₃), 24.0, 24.3, 25.3, 25.6 (CH(CH₃)₂), 25.1 (β -CH₂ (thf)), 27.9, 28.1 (CH(CH₃)₂), 69.6 (α -CH₂ (thf)), 82.6 (C9 (Flu)), 90.5 (N = CCH₃), 114.9, 118.2, 119.6, 122.7, 123.4, 123.9, 125.7, 128.1 (CH, Ar-C), 119.3, 123.6, 127.6, 133.5, 138.0, 143.2, 143.7, 149.1, 156.6, 179.2 ppm (quat. C (Ar) and quat. C (N = CC)); IR (Nujol, KBr): $\tilde{\nu} = 3020$ (w), 1525 (m),

1300 (s), 1230 (m), 1180 (m), 1080 (m), 1000 (m), 920 (m), 860 (s), 830 (m), 780 (s), 740 (s), 730 (s), 710 (s), 660 cm^{-1} (m).

Crystal data for **4**: $\text{C}_{88}\text{H}_{112}\text{N}_4\text{OYb}$, $M_r = 1414.86$, triclinic, $P\bar{1}P\bar{1}$, $a = 13.0385(7)$, $b = 13.8866(7)$, $c = 21.9438(12)$ Å, $\alpha = 85.8100(10)$, $\beta = 87.4260(10)$, $\gamma = 69.0470(10)^\circ$, $V = 3699.8(3)$ Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.270 \text{ Mg m}^{-3}$, absorption coefficient 1.313^{-3} , $F(000)$ 1492, reflections collected 20549, independent reflections 12985, GOF 1.047, $R = 0.0330$, $wR2 = 0.0837$.

Crystal data for **5**: $\text{C}_{45}\text{H}_{56}\text{N}_2\text{OYb}$, $M_r = 813.96$, orthorhombic, $Pbca$, $a = 15.3796(10)$, $b = 17.1883(12)$, $c = 29.211(2)$ Å, $\alpha = 90.0$, $\beta = 90.0$, $\gamma = 90.0^\circ$, $V = 7721.9(9)$ Å³, $Z = 8$, $\rho_{\text{calcd}} = 1.400 \text{ Mg m}^{-3}$, absorption coefficient 2.458^{-3} , $F(000)$ 3344, reflections collected 57402, independent reflections 6812, GOF 0.948, $R = 0.0280$, $wR2 = 0.0540$. All crystallographic calculations were performed with the Bruker SHELXTL package.^[16] CCDC-241424 (**4**) and -241425 (**5**) contain 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 CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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