

Lithium Complex of an Abnormal Carbene

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Dedicated to the memory of Professor Hans Georg von Schnering

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A lithium complex of an abnormal carbene with the composition $[\text{H}_3\text{BC}\{\{\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\}_2\text{CHCLi}(\text{THF})_3\}]$ was synthesized by the lithiation reaction of the N-heterocyclic carbene borane adduct $\{\text{IPr}\cdot\text{BH}_3$, $\text{IPr} = [\text{C}\{\{\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\}\text{CH}\}_2]$ (**1**)

with *n*BuLi. The lithiated species was proven by NMR spectroscopy and unambiguously established by single-crystal X-ray structural analysis.

Introduction

In the last two decades, the chemistry of N-heterocyclic carbenes (NHCs) has developed tremendously after the milestone report of a thermodynamically as well as a kinetically stable carbene in the absence of moisture and oxygen by Arduengo et al. in 1991.^[1] This discovery initiated further studies devoted to the synthesis of new NHCs and to their use as ligands in transition-metal complexes.^[2,3] Many highly reactive compounds with low-valent elements that are stabilized with NHCs have been documented.^[4,5a] We also reported the NHC-stabilized dichlorosilylene and studied its reactivity.^[5] Depending on the availability of the lone pair of electrons on the five-membered imidazole ring, carbenes are classified as *normal carbenes* (A in Figure 1) and *abnormal carbenes* (B in Figure 1). Abnormal N-heterocyclic carbenes (aNHCs) are kinetically less stable than their normal isomers and possess strong electron-donating properties. Recently, Bertrand et al. reported on stable aNHC,^[6] and Robinson et al. described the lithium complex of a carbene with lithium coordination at the second and fourth position of the five-membered imidazole ring.^[7] Furthermore, they synthesized the Lewis acid adduct by coordinating two molecules of BH_3 each at the second and fourth position of the five-membered imidazole ring.^[8] The $\text{NHC}\cdot\text{BR}_3$ ($\text{R} = \text{H}$, aryl, alkyl) adduct finds wide-spread

applications in synthetic chemistry (ionic, organometallic, and radical reactions).^[9] Braunschweig et al. incorporated the $\text{NHC}\cdot\text{BH}_3$ adduct into the coordination sphere of transition metals to afford η^1 -end-on-coordinated borane complexes.^[10] Very recently, we reported a facile route to abnormal NHCs via NHC base-stabilized dichlorosilylenes.^[11] Inspired by the above results, we wanted to synthesize the lithium complex of an abnormal carbene by treating $\text{IPr}\cdot\text{BH}_3$ (**2**) with *n*BuLi to lithiate the fourth position of the five-membered imidazole ring. The reaction proceeds as expected, and herein we report on the lithiated species of an $\text{IPr}\cdot\text{BH}_3$ adduct, with the composition $[\text{H}_3\text{BC}\{\{\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\}_2\text{CHCLi}(\text{THF})_3\}]$ (**3**). The formation of **3** was proven by NMR spectroscopy and unambiguously established by single-crystal X-ray structural analysis.

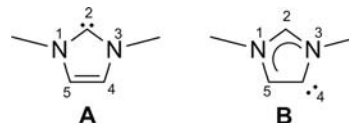
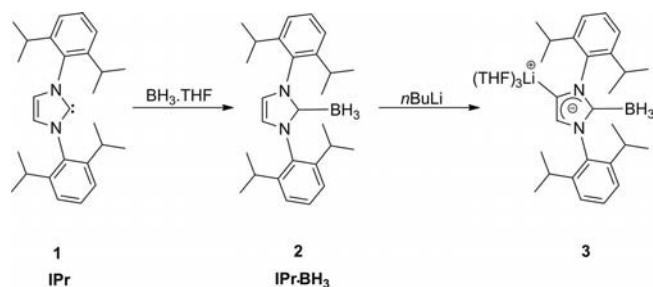


Figure 1. Schematic representation of normal carbene (A) and abnormal carbene (B).

Results and Discussion

The reaction of equimolar amounts of $\text{IPr}\cdot\text{BH}_3$ (**2**) with *n*BuLi afforded the lithiated species of $\text{IPr}\cdot\text{BH}_3$ with the composition $[\text{H}_3\text{BC}\{\{\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\}_2\text{CHCLi}(\text{THF})_3\}]$ (**3**) in quantitative yield (Scheme 1). Compound **3** is a colorless crystalline solid with good solubility in THF and has been characterized by NMR spectroscopy and single-crystal X-ray structural studies.

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Scheme 1. Synthesis of **3**.

The formation of the lithiated species **3** was readily noticed in the ^1H NMR spectrum. Compound **3** shows an upfield resonance for the imidazole ring hydrogen atom at $\delta = 6.18$ ppm in $[\text{D}_8]\text{THF}$ relative to that for **2** ($\delta = 7.26$ ppm).^[7] Moreover, the $\text{CH}(\text{CH}_3)_2$ protons in **3** display three resonances [$\delta = 1.05$ (6 H), 1.08 (6 H), and 1.16 ppm (12 H)], whereas **2** exhibits two resonances [$\delta = 1.17$ (12 H) and 1.26 ppm (12 H)] in the related ^1H NMR spectra. Further, the $\text{CH}(\text{CH}_3)_2$ proton in **3** resonates at $\delta = 2.73$ (2 H) and 2.84 ppm (2 H), while that of **2** resonates at $\delta = 2.61$ ppm (4 H). The ^7Li NMR spectrum shows a single resonance at $\delta = 0.64$ ppm. The ^{11}B NMR spectrum of **3** exhibits a resonance at $\delta = -35.59$ ppm and displays a quartet resonance with an intensity of 1:3:3:1, which indicates the coupling of the hydrogen atoms to the boron atom in the BH_3 unit ($J_{\text{BH}} = 85$ Hz). In addition, the structure of compound **3** was unambiguously established by low-temperature single-crystal X-ray structure analysis.

The molecular structure of **3** is displayed in Figure 2. Compound **3** crystallizes in the triclinic space group $P\bar{1}$. In **3**, the lithium is four coordinate and has a distorted tetrahe-

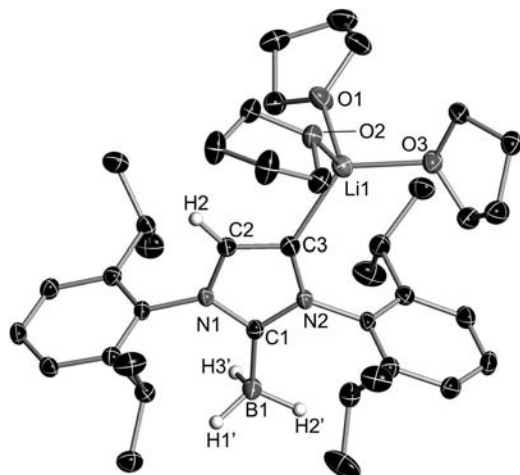


Figure 2. Molecular structure of **3**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity, with the exception of those for the BH_3 moiety and H(2). Selected bond lengths [Å] and angles [°]: Li(1)–C(3) 2.123(3), Li(1)–O(1) 1.993(2), Li(1)–O(2) 1.986(2), Li(1)–O(3) 1.969(2), B(1)–C(1) 1.6041(19); O(3)–Li(1)–O(2) 99.43(11), O(3)–Li(1)–O(1) 107.19(12), O(2)–Li(1)–O(1) 105.44(12), O(3)–Li(1)–C(3) 126.95(13), O(2)–Li(1)–C(3) 108.56(11), O(1)–Li(1)–C(3) 107.36(11).

dral geometry. The coordination environment consists of three oxygen atoms from the THF solvent molecules and one imidazole carbon atom of the carbene moiety. The Li–O_{av} and Li(1)–C(3) bond lengths are 1.983 and 2.122(3) Å, respectively, which is quite comparable to the bond lengths reported in the literature.^[12] The boron atom is also four coordinate^[13] and has a distorted tetrahedral geometry that comprises three hydrogen atoms and one carbon atom. The carbon–boron bond length in **3** is 1.6041(19) Å.

Conclusions

In this study, we report on the synthesis of a lithium complex of an abnormal carbene. The functionalization of the carbon atom of the imidazole ring at the fourth position with lithium is an interesting concept. This allows further modifications of the electronic and steric properties through a transmetalation process, which is currently under investigation.

Experimental Section

General: All manipulations were carried out in an inert atmosphere of dinitrogen by using standard Schlenk techniques and in a dinitrogen-filled glove box. Solvents were purified by the MBRAUN solvent purification system MB SPS-800. All chemicals were purchased from Aldrich and used without further purification. Compounds **1** and **2** were prepared as reported in the literature.^[14] ^1H , ^7Li , and ^{11}B NMR spectra were recorded with a Bruker Avance DPX 200, a Bruker Avance DRX 300, or a Bruker Avance DRX 500 spectrometer, by using $[\text{D}_8]\text{THF}$ as solvent. Chemical shifts δ are given relative to SiMe_4 . EI-MS spectra were obtained by using a Finnigan MAT 8230 instrument. Melting points were measured in a sealed glass tube on a Büchi B-540 melting point apparatus.

Synthesis of 3: To a solution of **2** (0.50 g, 4.10 mmol) in THF (60 mL) was added an $n\text{BuLi}$ solution (1.0 M, 4.2 mL, 4.20 mmol) at -78°C . The mixture was then allowed to come to room temperature and stirred for 12 h. Finally, the solution was filtered, and the solvent was removed in vacuo and evaporated to dryness to obtain the pure colorless crystalline solid of **3** (0.72 g, 93.22%). Mp: 112–115 $^\circ\text{C}$ (dec). ^1H NMR (200 MHz, $[\text{D}_8]\text{THF}$, 25°C): $\delta = 1.05$ [d, $J = 6.92$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$], 1.08 [d, $J = 6.9$ Hz, 6 H, $\text{CH}(\text{CH}_3)_2$], 1.16 [d, $J = 6.9$ Hz, 12 H, $\text{CH}(\text{CH}_3)_2$], 2.73 [m, 2 H, $\text{CH}(\text{CH}_3)_2$], 2.84 [m, 2 H, $\text{CH}(\text{CH}_3)_2$], 6.18 (s, 1 H, CH), 7.02 – 7.19 (m, 6 H, ArH) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.29 MHz, $[\text{D}_8]\text{THF}$, 25°C): $\delta = 22.86$ [$\text{CH}(\text{CH}_3)_2$], 23.07 [$\text{CH}(\text{CH}_3)_2$], 24.22 [$\text{CH}(\text{CH}_3)_2$], 24.38 [$\text{CH}(\text{CH}_3)_2$], 24.86 [$\text{CH}(\text{CH}_3)_2$], 25.03 [$\text{CH}(\text{CH}_3)_2$], 28.06 [$\text{CH}(\text{CH}_3)_2$], 28.15 [$\text{CH}(\text{CH}_3)_2$], 122.10 , 123.57 , 127.21 , 127.50 , 129.54 , 135.21 , 138.08 , 143.86 , 145.61 , 145.92 (NCH, NCLi, aromatic) ppm. $^{11}\text{B}\{^1\text{H}\}$ NMR (96.29 MHz, $[\text{D}_8]\text{THF}$, 25°C): $\delta = -35.59$ (q, $J_{\text{BH}} = 85$ Hz, BH_3) ppm. $^7\text{Li}\{^1\text{H}\}$ NMR (116.64 MHz, $[\text{D}_8]\text{THF}$, 25°C): $\delta = 0.64$ ppm.

Crystallography: Colorless crystals suitable for single-crystal X-ray analysis were obtained by storing **3** in THF solution at -32°C for 3 d. A shock-cooled crystal was selected and mounted under nitrogen atmosphere by using the device X-TEMP2.^[15] The data set was collected on an INCOATEC microfocus source with a mirror optics

instrument equipped with a Bruker Apex II detector (Mo- K_{α} radiation, $\lambda = 0.71073 \text{ \AA}$, 101 K).^[16] The integration was performed with SAINT V7.68A,^[17] which was followed by an empirical absorption correction with SADABS 2008/2.^[18] The structures were solved by direct methods (SHELXS) and refined against F^2 by using full-matrix least-squares methods with SHELXL.^[19] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions by using a riding model; their U_{iso} values were constrained to 1.5 U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms with the exception of H1', H2', H3' at B1 and H2, which was found freely.

Crystal Data for 3: $\text{C}_{39}\text{H}_{62}\text{BLiN}_2\text{O}_3$, $M_r = 624.66$, $0.2 \times 0.1 \times 0.05 \text{ mm}$, $a = 10.369(2)$, $b = 10.965(2)$, $c = 18.731(3) \text{ \AA}$, $\alpha = 73.74(2)^\circ$, $\beta = 89.37(3)^\circ$, $\gamma = 69.21(2)^\circ$, $V = 1902.0(6) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd.}} = 1.091 \text{ Mg/m}^3$, $\mu (\text{Mo-}K_{\alpha}) = 0.067 \text{ mm}^{-1}$, $2\theta_{\text{max}} = 50.7^\circ$, 40602 reflections measured, 6982 independent ($R_{\text{int}} = 0.029$), $R1 = 0.0387$ [$I > 2\sigma(I)$], $wR2 = 0.0960$ (all data), residual density peaks: 0.242 to $-0.219 \text{ e \AA}^{-3}$. CCDC-826662 contains the supplementary crystallographic data for 3. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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- [1] A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363.
- [2] a) S. P. Nolan (Ed.), *N-Heterocyclic Carbenes in Synthesis*, Wiley-VCH, Weinheim, Germany, **2006**; b) F. Glorius (Ed.), *N-Heterocyclic Carbenes in Transition Metal Catalysis*, Springer-Verlag, Berlin, **2007**; c) J. Chun, I. G. Jung, H. J. Kim, M. Park, M. S. Lah, S. U. Son, *Inorg. Chem.* **2009**, *48*, 6353–6355; d) P.-C. Chiang, M. Rommel, J. W. Bode, *J. Am. Chem. Soc.* **2009**, *131*, 8714–8718; e) V. J. Catalano, A. L. Moore, J. Shearer, J. Kim, *Inorg. Chem.* **2009**, *48*, 11362–11375; f) N. D. Harrold, R. Waterman, G. L. Hillhouse, T. R. Cundari, *J. Am. Chem. Soc.* **2009**, *131*, 12872–12873; g) A. Sinha, S. M. W. Rahaman, M. Sarkar, B. Saha, P. Daw, J. K. Bera, *Inorg. Chem.* **2009**, *48*, 11114–11122; h) A. G. Tennyson, E. L. Rosen, M. S. Collins, V. M. Lynch, C. W. Bielawski, *Inorg. Chem.* **2009**, *48*, 6924–6933; i) Y. Lee, B. Li, A. H. Hoveyda, *J. Am. Chem. Soc.* **2009**, *131*, 11625–11633; j) P. M. Zimmerman, A. Paul, C. B. Musgrave, *Inorg. Chem.* **2009**, *48*, 5418–5433; k) S. Groysman, R. H. Holm, *Inorg. Chem.* **2009**, *48*, 621–627; l) E. M. Phillips, M. Riedrich, K. A. Scheidt, *J. Am. Chem. Soc.* **2010**, *132*, 13179–13181; m) M. K. Samantaray, C. Dash, M. M. Shaikh, K. Pang, R. J. Butcher, P. Ghosh, *Inorg. Chem.* **2011**, *50*, 1840–1848; n) J. Mathew, C. H. Suresh, *Inorg. Chem.* **2010**, *49*, 4665–4669; o) J. M. Smith, J. R. Long, *Inorg. Chem.* **2010**, *49*, 11223–11230; p) K. Hirai, T. Itoh, H. Tomioka, *Chem. Rev.* **2009**, *109*, 3275–3332; q) F. E. Hahn, M. C. Jahnke, *Angew. Chem.* **2008**, *120*, 3166–3216; *Angew. Chem. Int. Ed.* **2008**, *47*, 3122–3172; r) M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem.* **2010**, *122*, 8992–9032; *Angew. Chem. Int. Ed.* **2010**, *49*, 8810–8849; s) L. Mercks, M. Albrecht, *Chem. Soc. Rev.* **2010**, *39*, 1903–1912.
- [3] a) D. P. Mills, L. Soutar, W. Lewis, A. J. Blake, S. T. Liddle, *J. Am. Chem. Soc.* **2010**, *132*, 14379–14381; b) C.-H. Yang, J. Beltran, V. Lemaire, J. Cornil, D. Hartmann, W. Sarfert, R. Fröhlich, C. Bizzari, L. D. Cola, *Inorg. Chem.* **2010**, *49*, 9891–9901; c) H.-J. Park, K. H. Kim, S. Y. Choi, H.-M. Kim, W. I. Lee, Y. K. Kang, Y. K. Chung, *Inorg. Chem.* **2010**, *49*, 7340–7352; d) R. S. Crees, M. L. Cole, L. R. Hanton, C. J. Sumbly, *Inorg. Chem.* **2010**, *49*, 1712–1719; e) C. Dash, M. M. Shaikh, R. J. Butcher, P. Ghosh, *Inorg. Chem.* **2010**, *49*, 4972–4983; f) C.-F. Fu, C.-C. Lee, Y.-H. Liu, S.-M. Peng, S. Warsink, C. J. Elsevier, J.-T. Chen, S.-T. Liu, *Inorg. Chem.* **2010**, *49*, 3011–3018; g) S. Naeem, L. Delaude, A. J. P. White, J. D. E. T. Wilton-Ely, *Inorg. Chem.* **2010**, *49*, 1784–1793; h) W.-Q. Zhang, A. C. Whitwood, I. J. S. Fairlamb, J. M. Lynam, *Inorg. Chem.* **2010**, *49*, 8941–8952; i) F. Huang, G. Lu, L. Zhao, Z.-X. Wang, *J. Am. Chem. Soc.* **2010**, *132*, 12388–12396; j) C.-H. Hsieh, M. Y. Darensbourg, *J. Am. Chem. Soc.* **2010**, *132*, 14118–14125; k) O. Schuster, L. Yang, H. G. Raubenheimer, M. Albrecht, *Chem. Rev.* **2009**, *109*, 3445–3478; l) P. Arnold, S. Pearson, *Coord. Chem. Rev.* **2007**, *251*, 596–609; m) M. Albrecht, *Chem. Commun.* **2008**, 3601–3610; n) K. E. Krahulic, H. M. Tuononen, M. Parvez, R. Roesler, *J. Am. Chem. Soc.* **2009**, *131*, 5858–5865; o) L. Benhamou, E. Chardon, G. Lavigne, S. Bellemine-Laponnaz, V. César, *Chem. Rev.* **2011**, *111*, 2705–2733.
- [4] a) B. Quillian, P. Wei, C. S. Wannere, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2009**, *131*, 3168–3169; b) Y. Wang, Y. Xie, P. Wei, R. B. King, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *Science* **2008**, *321*, 1069–1071; c) Y. Wang, G. H. Robinson, *Chem. Commun.* **2009**, 5201–5213.
- [5] a) R. S. Ghadwal, H. W. Roesky, S. Merkel, J. Henn, D. Stalke, *Angew. Chem.* **2009**, *121*, 5793–5796; *Angew. Chem. Int. Ed.* **2009**, *48*, 5683–5686; b) J. Li, S. Merkel, J. Henn, K. Meindl, A. Döring, H. W. Roesky, R. S. Ghadwal, D. Stalke, *Inorg. Chem.* **2010**, *49*, 775–777; c) G. Tavčar, S. S. Sen, R. Azhakar, A. Thorn, H. W. Roesky, *Inorg. Chem.* **2010**, *49*, 10199–10202; d) R. Azhakar, G. Tavčar, H. W. Roesky, J. Hey, D. Stalke, *Eur. J. Inorg. Chem.* **2011**, 475–477; e) R. Azhakar, S. P. Sarish, G. Tavčar, H. W. Roesky, J. Hey, D. Stalke, D. Koley, *Inorg. Chem.* **2011**, *50*, 3028–3036; f) R. S. Ghadwal, K. Pröpper, B. Dittich, P. G. Jones, H. W. Roesky, *Inorg. Chem.* **2011**, *50*, 358–364.
- [6] E. Aldeco-Parez, A. J. Rosenthal, B. Donnadieu, P. Parameswaran, G. Frenking, G. Bertrand, *Science* **2008**, *321*, 1069–1071.
- [7] Y. Wang, Y. P. Xie, M. Y. Abraham, P. Wei, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2010**, *132*, 14370–14372.
- [8] Y. Wang, Y. P. Xie, M. Y. Abraham, P. Wei, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *Organometallics* **2011**, *30*, 1303–1306.
- [9] a) D. M. Lindsay, D. McArthur, *Chem. Commun.* **2010**, 2474–2476; b) J. Monot, M. M. Brahmi, S.-H. Ueng, C. Robert, M. D.-E. Murr, D. P. Curran, M. Malacria, L. Fensterbank, E. Lacote, *Org. Lett.* **2009**, *11*, 4914–4917; c) S.-H. Ueng, M. M. Brahmi, E. Derat, L. Fensterbank, E. Lacote, M. Malacria, D. P. Curran, *J. Am. Chem. Soc.* **2008**, *130*, 10082–10083.
- [10] P. Bissinger, H. Braunschweig, T. Kupfer, K. Radacki, *Organometallics* **2010**, *29*, 3987–3990.
- [11] R. S. Ghadwal, H. W. Roesky, M. Granitzka, D. Stalke, *J. Am. Chem. Soc.* **2010**, *132*, 10018–10020.
- [12] T. Stey, D. Stalke, “Lead Structures in Lithium Organic Chemistry” in *The Chemistry of Organolithium Compounds* (Eds.: Z. Rappoport, I. Marek), John Wiley & Sons, Chichester, United Kingdom, **2004**, pp. 47–120.

- [13] A. Jana, D. Leusser, I. Objartel, H. W. Roesky, D. Stalke, *Dalton Trans.* **2011**, 40, 5458–5463.
- [14] Y. Wang, B. Quillian, P. Wei, C. S. Wannere, Y. Xie, R. B. King, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2007**, 129, 12412–12413.
- [15] a) D. Stalke, *Chem. Soc. Rev.* **1998**, 27, 171–178; b) T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, 26, 615–619.
- [16] T. Schulz, K. Meindl, D. Leusser, D. Stern, J. Graf, C. Michaelson, M. Ruf, G. M. Sheldrick, D. Stalke, *J. Appl. Crystallogr.* **2009**, 42, 885–891.
- [17] Bruker *SAINT* v7.68A, WI, USA, Madison, **2009**.
- [18] G. M. Sheldrick, *SADABS 2008/2*, Göttingen, **2008**.
- [19] a) G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, 64, 112–122; b) G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, 46, 467–473.

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