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Heterobimetallic Bisphosphonate Titanium Complexes: Carbene-Like Carbanions?

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A new class of carbene-like titanium complexes is easily accessible by means of a dilithiation–transmetallation sequence of a bisphosphonate. The X-ray structure of the dimeric, organometallic compound **3** reveals a nano-sized, multi-layer aggregate with titanium-metallated, trigonal planar carbon centers being devoid of Li contacts. DFT calculations show that the metallated carbon is a carbanion with only a slight carbene portion (10 %); the carbene character can be easily strengthened or weakened by varying the counterion. We anticipate that the sensitivity and flexibility to influence the electronic character of these carbene-like carbanions offers a way to design new versatile reagents with variable chemical properties.

Introduction

The successful application of carbenes in various areas such as catalysis and organic synthesis has driven the development to systematic and rational approaches for their preparation.[1] Novel carbene complexes are expected to possess superior properties compared to traditional Fischer- or Schrock-type carbene complexes.

Our impetus for the synthesis of related complexes with a modified carbene nature was initiated from our observation, that the formation of heterobimetallic phosphonates, sulfoximines and sulfones, generated in the reaction of geminal organodimetallics with transitionmetal halides, are leading to organometallic species with an unusual behaviour; they resemble species lying between carbanions and carbenes.[2] As for the novel carbene complexes the synthetic access is achieved via a geminal dianion followed by transmetallation. However, contrary to a typical metal carbene species which is characterized by a carbon–metal double bond, a full negative charge remains formally at the carbon center balanced by an external Li cation. The control of the nucleophilicity and reactivity of such an intermediary carbene-like carbanion is achieved by choosing an appropriate organic ligand, e.g., a geminal carbodianion stabilized by one or two neighboring electron-withdrawing groups (EWG), and a transition metal on the carbene-like carbon. Especially the phosphorus-containing EWG groups showed to be suitable in this respect.[2a,3]

Here we present the synthesis and characterization of the first heterobimetallorganic carbene-like complex with a bisphosphonate ligand; the metal center is titanium(IV). Besides addressing the fundamental question concerning the electronic structure of the titanium–carbon bond in such heterobimetallic complexes we use the predictive power of DFT calculations to elucidate how the character of this bond can be directed towards carbene or carbanion.

Results and Discussion

Dilithiation of bisphosphonate **1** with 2.2 equiv. *n*BuLi in diethyl ether, followed by addition of [ClTi(O*i*Pr)$_3$], lead, after filtration of the turbid solution, to the lithium–titanium bisphosphonate **3** as yellow crystals in 34 % yield. **3** consists of two monolithiated titanium-bisphosphonate complex units including two molecules of LiCl and Li[Ti(O*i*Pr)$_5$].

The center of the aggregate **3** is a (Li–Cl)$_2$ four-membered ring (Li1–Cl1–Li1′–Cl1′, see Figure 1) serving as an aggregation nucleus for crystallization. Each lithium atom of this ring is coordinated by two phosphonate oxygens in a bidentate fashion inducing six membered ring motifs with the atomic sequence Li1–O1–P1–Cα–P2–O4 (or the symmetry related sequence Li1′–O1′–P1′–Cα′–P2′–O4′; in the text that follows any symmetry related motifs will not be mentioned anymore). The chloride anions are surrounded by four lithium cations forming a square pyramid with the anion on top and a lithium-containing square at the bottom (Scheme 1).

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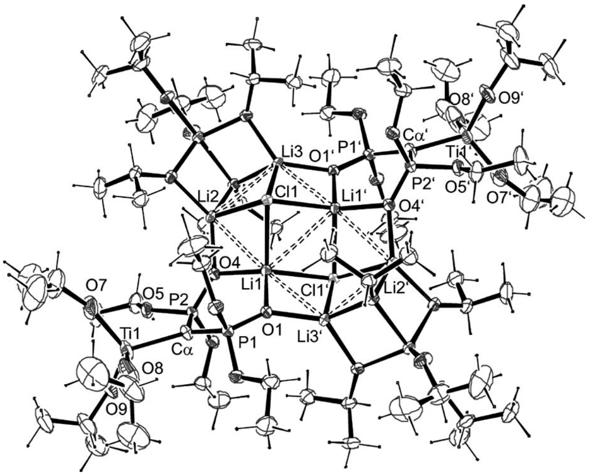
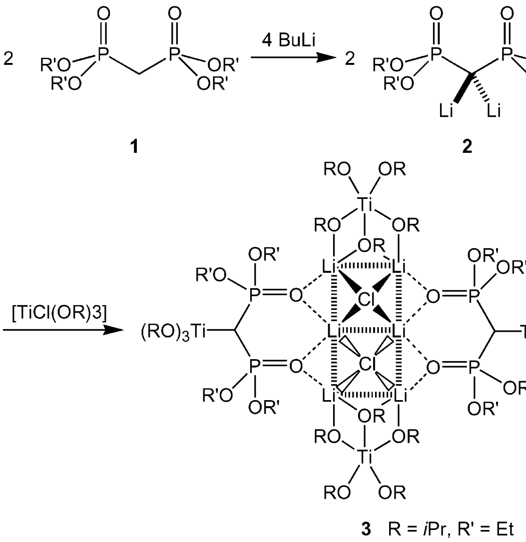


Figure 1. ORTEP plot of the centrosymmetric aggregate **3**. The numbering matches that of Scheme 1. Ellipsoids are drawn at the 20% probability level.[4]



Scheme 1.

Tetracoordination of Ti1 induces a distorted tetrahedral geometry in the titanium-bisphosphonate units. The tetrahedral positions are occupied by the three isopropylate O-atoms O7, O8, O9, and the Cα-atom of the bisphosphonate. The ethoxy oxygen O5 of the phosphonate ester shows a weak coordination to the titanium atom Ti1 with a rather long Ti–O distance of 2.81(9) Å which is more than 1 Å longer than the Ti–O bonds of the isopropylate groups [1.737(3)–1.794(2) Å]. But this interaction is too weak to change the coordination geometry at the titanium atom, although a four-membered Ti1–Cα-P2–O5 ring chelate is formed, a structural feature similar to a lithium–titanium-silylphosphonate complex[2a] and to the carbene complex of a diphenylthiophosphinoyl-stabilized pincer ligand with zirconium.[4b]

The Ti1–Cα bond length in **3** is 2.055(2) Å, a distance comparable to that in a related lithium–titanium-phosphonate[2a] [2.00(1) Å] and a lithium–titanium sulfone[2c] [2.036(7) Å]. The P1–Cα and P2–Cα bond length of 1.690(3) Å and 1.677(3) Å are significantly shortened as compared to non-metallated phosphonates,[5] due to negative hyperconjugative interactions (see below).[3a–3c] The titanated anionic Cα-atom adopts essentially a triganal planar geometry, devoid of C–Li contacts, as it is known to be typical of lithiated phosphonates.[2,5] This planarization is supported by the sum of angles at Cα of 359°.

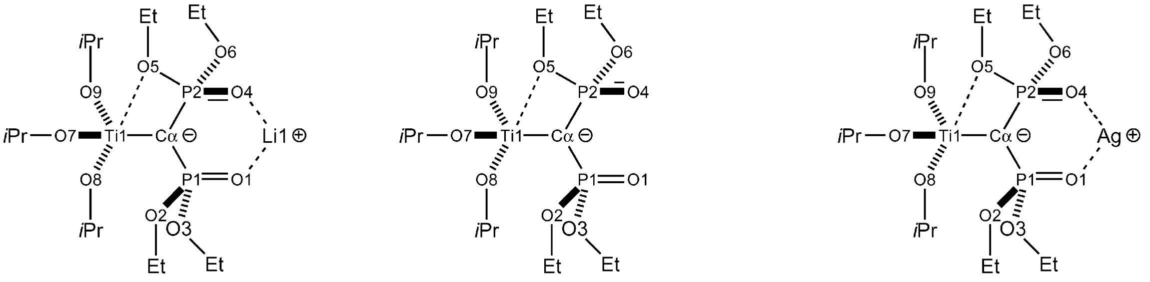
The ^{1}H-,^{13}C-, ^{7}Li- and ^{31}P-NMR spectra were recorded in [D$_8$]toluene to gain insight into the solution structure of **3**. The aggregation state cannot be assigned unambiguously. There is only one, broad signal in the ^{7}Li NMR spectrum centered at $\delta = -1.86$ ppm. We propose that **3** forms in apolar solution an aggregate similar to that in the X-ray structure with an apolar surface layer of isopropyl groups, an organometallic layer of titanium complexes, and a polar nuclei of lithium and chlorine ions. The network of ionic interactions in the aggregate center is of course less rigid in solution than in the X-ray allowing fast exchange. The resulting chemical shift signal for the lithium ions is broad and upfield-shifted with respect to the reference (LiCl) due to an increased shielding by the organometallic shell. Disaggregation of **3** leading to Li[Ti(O*i*Pr)$_3$(C(PO(OEt)$_2$)$_2$)] (**4**) (see Scheme 2), LiO*i*Pr, Ti(O*i*Pr)$_4$, and LiCl cannot be fully excluded. This would, however, imply that there is fast exchange between Li[Ti(O*i*Pr)$_3$(C(PO(OEt)$_2$)$_2$)] and LiO*i*Pr which seems to be unlikely in apolar toluene solution. Further NMR studies especially at lower temperatures are in preparation to clarify the aggregation state.

Whereas the ^{1}H NMR spectroscopic data showed only very broad resonances for the alkoxide protons, the examination by ^{13}C-NMR spectroscopy revealed some changes in chemical shifts on metallation. The most remarkable effect was observed for the Cα atom, which shifted downfield to δ = 137.8 ppm ($\Delta\delta$ = 112 ppm). Downfield shifting is a characteristic accompaniment of dilithiation–transmetallation sequences. For comparison, the dilithiation of a sulfone and a phosphonate and subsequent transmetallatation with titanium leads to a downfield shift of $\Delta\delta$ = 89 ppm and $\Delta\delta$ = 135 ppm, respectively, for the metallated Cα atom.[2a,2c]

Smaller changes upon metallation were noticed for the titanium chelating ethoxy C-atom, which suffers a downfield shift of $\Delta\delta$ = 11 ppm to approx. 76 ppm. We conclude that in solution the sp^2-character of Cα together with the Ti1–Cα bond is responsible for the strong downfield shift.

Further insights into the electronic structure of the Ti1–Cα bond are obtained from a density functional theory (DFT) study on the three model systems **4**, **5**, and **6**.

The three model systems differ by the complexation of the phosphonate oxygen atoms. In the crystal structure of **3** the phosphonate oxygen atoms O1 and O4 atoms are surrounded by three lithium ions (Li1, Li2, Li3′) and two chlorine ions (Cl1, Cl1′). To mimic this complexation we kept the lithium ion Li1 that complexes both phosphonate oxygen atoms in the X-ray structure, it neutralizes the negatively charged carbodianion–titanium complex (model system **4**). The influence of the lithium counterion (e.g., the change of the structure and its electronic properties upon



4 **5** **6**

Scheme 2.

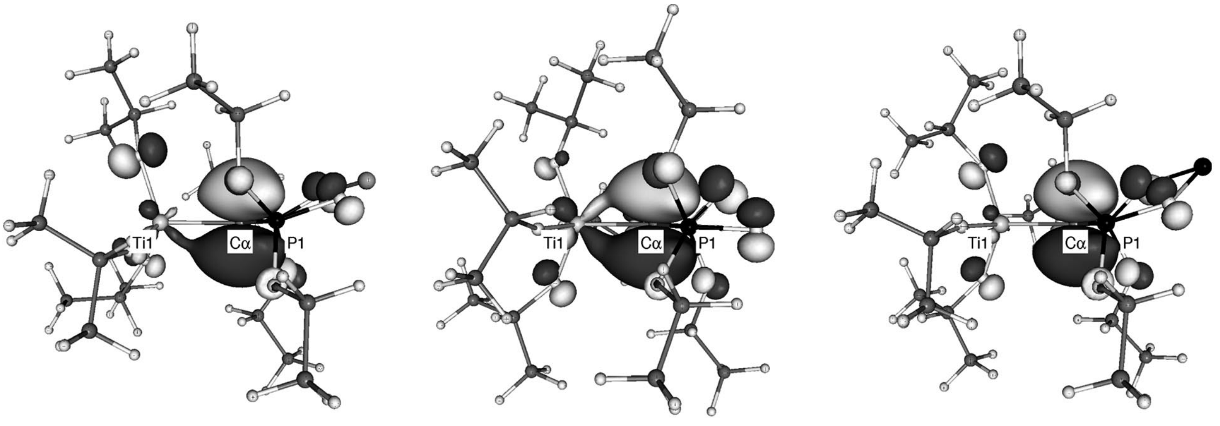
removal this counterion) was studied with model system **5**. And finally we wanted to investigate the effects that result when the hard lithium ion is replaced by a soft silver ion (model system **6**).

The minimized geometry at the carbon atom Cα of **4** is in good agreement with the X-ray structure.[9] The center remains planar, the sum of angles at Cα is 359.8°. The Ti1–Cα bond of 2.063 Å differs by less than 1 pm from the value of the crystal structure (2.055 Å). The P1–Cα and P2–Cα bonds are slightly longer in the minimized structure than in the X-ray structure (1.708 Å and 1.710 Å instead of 1.690 Å and 1.677 Å). The attractive interaction between the ethoxy oxygen O5 and Ti1 is, however, underestimated by the calculations, i.e., the distance between the two atoms is 3.200 Å and therefore more than 0.3 Å larger than in the X-ray structure (2.819 Å).

A bonding interaction between Cα and Ti1 is described by the third highest molecular orbital (not shown): a σ-bond is formed from a sp^2-orbital of the carbon atom and a d$_{z^2}$-orbital of the titanium atom. This bond is polarized towards the carbon atom. The contribution of the carbon atom, i.e., the sum of the squares of atomic orbital coefficients, to the σ-bond is twice as large than the contribution of the titanium atom. The highest occupied molecular orbital (HOMO) of **4** resembles a lone-pair at the carbon atom Cα (Figure 2) with a strong polarization towards both phosphorus atoms. The contribution of the two phosphorus atoms to the HOMO is three times smaller relative to the contribution of the carbon atom. There is also a slight polarization towards the Ti1 atom due to mixing with d-type orbitals of titanium; but the contribution of the titanium atom to the HOMO is more than ten times smaller than the contribution of the carbon atom.

We note, therefore, that the carbon center Cα is a carbanion with a slight carbene character of only about 10%. The same conclusion is obtained from the NBO analysis:[10] the Ti1–Cα σ-bond (population: 1.9) is formed by a combination of a sp$^{1.84}$-orbital of Cα (83%) and a d(s$^{0.15}$)-orbital of Ti1 (17%), and there is a lone-pair at carbon Cα that is purely described by a *p*-orbital (population: 1.6). The carbanionic character of Cα is also supported by ^{13}C NMR spectroscopy: the chemical shift of the metallated carbon atom (δ = 137.8 ppm) is in the characteristic range of lithium–titanium phosphonates;[2] and thus more than 50 ppm upfield shifted with respect to a veritable titanium carbene complex of a bisphosphoranimine-stabilized carbodianion.[3i] The upfield shift reflects the electron-enriched environment and the reduced carbene character of carbon atom Cα in **4**.

When the Li atom is removed from the model system we obtain a negatively charged carbodianion–titanium complex **5**. The minimized structure of **5** features a slightly



4 **5** **6**

Figure 2. The highest occupied molecular orbital (HOMO) of model systems **4**–**6**. The surfaces mark isodensities of –0.04 *e* (light gray) and 0.04 *e* (dark gray); they were drawn from Guassian03 cube-files with the program MOLEKEL.[11]

shorter Ti1–Cα bond (2.043 Å) than **4** and the P–C bonds increase slightly to 1.714 Å (P1–Cα) and 1.715 Å (P2–Cα). The distance for the coordination between Ti1 and O5 is now dramatically shorter (2.309 Å), even much shorter than in the X-ray structure (2.819 Å) of **3**. The HOMO shows a strong polarization towards the titanium atom (Figure 2). The contribution from the d-orbitals of the titanium to the HOMO of **5** is twice as high as in **4**. The increased carbene character is in agreement with the observed shorter Ti–C bond in **5** as compared to **4**. The NBO analysis shows now in addition to the σ-bond a strongly polarized, doubly occupied π-bond that is formed by a pure *p*-orbital of Cα (87%) and a pure d-orbital of Ti1 (13%). The smaller carbanionic character of **5** in comparison to **4** can be rationalized by the missing stabilization due to the positively charged counterion.

The replacement of the hard lithium ion (model system **4**) by the softer silver ion (**6**) leads to a longer Ti1–Cα bond (2.088 Å) and shorter P–C bonds (1.698 Å). In addition the coordination of O5 becomes significantly stronger (2.455 Å) but it is still less strong than in **5**. The HOMO shows almost no polarization, i.e., the contributions of the phosphorus and titanium atoms are 5 times (P) and 20 times (Ti) smaller relative to the contribution of the carbon atom. The substitution of the counterion has cancelled the carbene character and the carbon center is now a pure carbanion. The increase of the Ti1–Cα bond underlies this change in the electronic structure. The larger carbanionic character of **6** in comparison to **4** can be explained by a higher stabilization of the lone-pair in **6** due to a stronger hyperconjugative interaction of the lone pair *p*-orbital with the σ*-orbitals of the P–O(phosphonate ester) bonds: the second-order perturbation analysis of the Fock matrix in NBO basis predicts a stabilizing effect for this interaction of 21.3 $\text{kcal}\,\text{mol}^{-1}$ for **6** and only 15.9 $\text{kcal}\,\text{mol}^{-1}$ for **4**. This stronger negative hyperconjugation explains also the shortening of the P–C bonds.

Conclusions

Double deprotonated bisphosphonates are capable of forming stable organobimetallic complexes with titanium(IV). The resulting metallated carbon center is best described as a carbene-like carbanion, i.e., a carbanion with a slight carbene character.

In comparison to dilithiated geminal dicarbanions[3b] the substitution of one of the alkali metals by a transition metal has introduced a slight carbene character. This can be deduced from the planarity of the carbon center and the length of the carbon–titanium bond that lies between a single and a double bond. The slight carbene character is also confirmed from DFT calculations where the HOMO resembles a *p*-orbital of the carbon atom with a slight polarization towards the titanium (similar to a π-orbital).

The carbene character of heterobimetallic **3** is, however, much smaller with respect to existing typical carbene complexes formed from geminal dicarbanions and transition metals with two leaving groups (e.g., two or more halides).[3a,3i] This is supported by the rather long titanium–carbon bond (2.055 Å) and the very low chemical shift of Cα (δ =137.8 ppm). The use of a transition metal with only a single halide leaving group (and a second alkali metal as counterion) "freezes" the property of **3** on a intermediate carbanion-carbene level. From all known dianion transition metal complexes the heterobimetallic complex **3** is the one with the lowest carbene character; it is also lower than in analogous heterobimetallic titanium complexes of sulfonate- and phosphate-stabilized geminal dicarbanions.[2a,2c]

The transmetallation allows to combine the property of a carbene with that of a carbanion to form a carbene-like carbanion. Calculations suggest that the carbene character in such heterobimetallic compounds can easily be strengthened or weakened by the variation of the counterion. This offers a promising way to vary the nucleophilicity and reactivity.

Such carbene-like carbanions are supposed to possess a new ambivalent chemical behaviour and therefore may be applied as reagent in various classes of reactions, such as classical metal carbene-type reactions like insertions and cyclopropanations; regarding the latter, the electron-rich "carbene" **3** seems to be ideally suited for electron-poor alkenes like α,β-unsaturated carbonyl substrates. Due to its dominant nucleophilic character the reagent **3** might also be used in nucleophilic additions. Of special interest to us is the influence of the transition metal of the attacking carbanion in HWE reactions[13] Our future experimental studies will focus on the testing of this novel reagent in synthesis reactions and elucidate the variability of their electronic properties. Calculations, on the other hand, will investigate the role of the transition metal, i.e., how does the exchange of the transition metal, for example substitution of titanium(IV) by zirconium(IV), influences the electronic structure of these carbene-like carbanions.

Experimental Section

Synthesis of 3: A solution of **1** (100 mg, 0.43 mmol) in diethyl ether (2 mL) was treated with *n*BuLi in hexane (0.60 mL, 1.58 M, 0.95 mmol) at –78 °C. Stirring for 2 h at 0 °C was followed by addition of a solution of $[\text{TiCl}(\text{O}i\text{Pr})_3]$ in 2 mL of diethyl ether (112 mg, 0.43 mmol). After filtration of the turbid solution the remaining liquid was concentrated in vacuo and stored for 24 h at –20 °C until yellow crystals of **3**, suitable for X-ray analysis, were grown (122 mg, 34%).

^{1}H NMR (500 MHz, [D$_8$]toluene, 25 °C): δ = 1.15–1.25 (m, 42 H, CH_3), 3.57–4.05 (m, 26 H, OCH_2, O*i*Pr), 4.46–4.72 ppm (m, 6 H, O*i*Pr). ^{13}C NMR (125 MHz, [D$_8$]toluene, 25 °C): δ = 16.56, 16.97, 17.08, 20.02, 20.21, 21.65, 25.08, 25.24, 25.40, 25.56, 25.72, 25.89, 26.33, 27.14, 27.34, 27.91, 60.49, 60.68, 61.02, 61.60, 67.16, 67.33, 67.51, 67.68, 67.86, 68.03, 72.33, 74.46, 75.30, 76.40, 76.83, 137.8 ppm. ^{31}P NMR (202 MHz, [D$_8$]toluene, 25 °C, $(\text{PhO})_3\text{PO}$): δ = 41.48, 38.90 ppm. ^{7}Li NMR (194 MHz, [D$_8$]toluene, 25 °C, LiCl): δ = –1.86 ppm.

Computational Details: The calculations were performed with the program package Gaussian03[12] using the hybrid-functional

B3LYP and the basis set 6-311+G* for the central carbon atom Cα and all oxygen and phosphorus atoms, the basis set DGDPZ for the metals Ti and Ag, and the standard basis set 6-31G* for all other atoms (propyl and ethyl groups, Li atom). The X-ray geometry served as starting point for the minimizations. All systems were studied in their singlet state.

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[4] X-ray crystal data for **3**: $C_{68}H_{162}Cl_2Li_6O_{29}P_4Ti_4$, $M_r = 1748.15$, monoclinic, space group $C\ 2/c$, $a = 30.5054(7)$ Å, $b = 17.9005(5)$ Å, $c = 21.8176(4)$ Å, $\alpha = 90°$, $\beta = 114.4919(14)°$, $\gamma = 90°$, $V = 10841.8$ Å^3, $Z = 4$, $F(000) = 3768$, $\rho = 1.071\ \mathrm{kg\,m^{-3}}$, $\mu = 0.453\ \mathrm{mm^{-1}}$, crystal dimensions = $0.10 \times 0.22 \times 0.32$ mm, $T = 193$ K, radiation Mo-K_α ($\lambda = 0.71073$ Å), scan type $\omega/2\Theta$, $\Theta_{max} = 27.47°$, number of measured reflections: 44530, number of independent reflections: 21946, number of reflections in refinement: 13193, $I > 3.00\sigma(I)$, number of parameters: 529, $R = 0.0682$, $R_w = 0.0359$, weighting scheme $\omega\cdot[1 - (\delta F/6\sigma F)^2]^2$, $\Delta\rho$ 1.24/–0.63 eÅ^{-3}, $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$, $R_w = [\Sigma(|F_o| - |F_c|)^2\cdot\omega/\Sigma F_o{}^2\cdot\omega]^{1/2}$. Crystals were stuck with perfluoropolyether to a glass fibre, mounted on the diffractometer and cooled with an Oxford Cryostream to 193 K. Data collection has been carried out using a Nonius KappaCCD area detector equipped with a graphite monochromator. The structure was solved by direct methods with the program SIR92.[6] Anisotropic least-squares full-matrix refinement was carried out on all non-hydrogen atoms using the program CRYSTALS.[7] The positions of the hydrogen atoms have been determined geometrically. Chebychev polynomial weights have been used to complete the refinement.[8] Scattering factors have been taken from the International Tables, vol. IV, Table 2.2B. CCDC-204453 contains the supplementary crystallographic data for compound **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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