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Disclosing Cyclic(Alkyl)(Amino)Carbenes as One-Electron Reductants: Synthesis of Acyclic(Amino)(Aryl)Carbene-Based Kekulé Diradicaloids

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Dedicated to Professor A. Ajayaghosh on the occasion of his 60th birthday

Abstract: Herein, we disclose cyclic(alkyl)(amino)carbenes (CAACs) to be one-electron reductants under the formation of a transient radical cation as indicated by EPR spectroscopy. The disclosed CAAC reducing reactivity was used to synthesize acyclic(amino)(aryl)carbene-based Thiele and Chichibabin hydrocarbons, a new class of Kekulé diradicaloids. The results demonstrate CAACs to be potent organic reductants. Notably, the acyclic(amino)(aryl)carbene-based Chichibabin's hydrocarbon shows an appreciable population of the triplet state at room temperature, as evidenced by both variable-temperature NMR and EPR spectroscopy.

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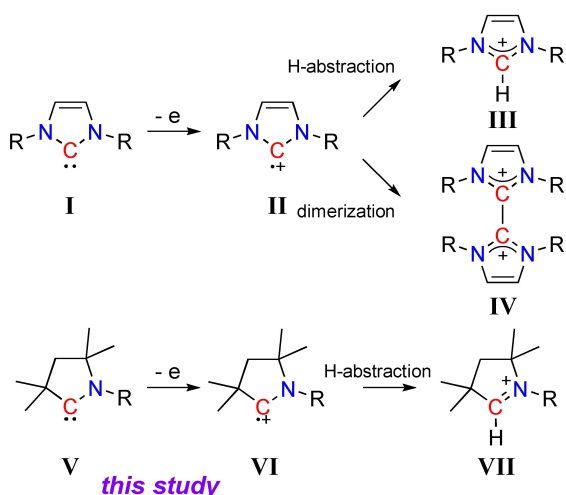
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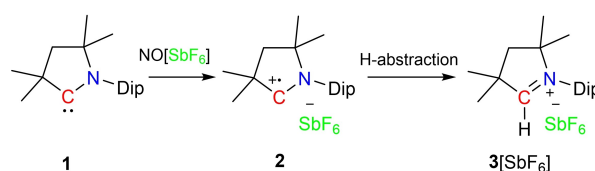💻 Supporting information for this article is available on the WWW under https://doi.org/10.1002/chem.202104567

Introduction

Since the report of cyclic(alkyl)(amino)carbenes (CAACs) in 2005 by Bertrand's group[1] such carbenes have been vastly used in different research areas ranging from advanced synthetic chemistry,[2] organometallic chemistry[3] to catalysis[4] and material chemistry.[5] In most cases it has been used as Lewis base, that is, a two-electron σ-donor accompanied by π-acceptor properties. In comparison with N-heterocyclic carbenes (NHCs), CAACs are considered as both more nucleophilic (stronger σ-donors) as well as more electrophilic (stronger π-acceptors) in nature due to the differences in substitution at the carbenic carbon center: two electronegative/π-donating amino substituents versus one electronegative/π-donating amino substituent and one σ-donating alkyl group.[6] On the other hand, CAACs have a relatively smaller singlet-triplet energy gap compared to NHCs.[6] As a result, CAACs are known to share one-electron with a reaction partner to form a covalent bond under the formation of various compounds including C-center based diradicals.[7] However, unlike for NHCs the formation of radical-cations of CAACs have not been reported, not even in reactions with $Ph_3C^+X^-$ (X=PF_6 and $B(C_6F_5)_4$)[8] or $B(C_6F_5)_3$.[9] In the case of NHCs **I** the formation of radical cations **II** (Scheme 1) was observed with various oxidizing reagents.[10] Recently, the formation of NHC-derived radical cations **II** and respective single electron transfer events were studied comprehensively by UV/Vis spectroscopy.[11] NHC-derived radical cations have limited stability; either they abstract available hydrogen atoms to yield **III** or they dimerize to the dication of NHC-NHC dimer **IV** (Scheme 1), based on the N-substituents.[10] The radical cations of parent carbenes (CH_2) as well as diaryl carbenes have been of particular interest for a long time during which they have been studied as transient species.[12] Thus, we were

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Scheme 1. One-electron oxidation of *N*-heterocyclic carbene **I** (top) and cyclic(alkyl)(amino)carbene **V** (bottom) (R = monoanionic organic substituent and the counter anions are omitted for clarity).

Scheme 2. Oxidation of **1** (Dip = 2,6-*i*Pr$_2$C$_6$H$_3$).

Results and Discussion

For this study, CAAC **1** (Figure 1) was chosen and the investigation of its one-electron oxidation first addressed through electrochemical methods. The cyclic voltammogram (CV) of **1** exhibits an irreversible anodic peak potential which is similarly pronounced in the oxidative differential pulse voltammogram (DPV; Figure 1a, insert).[17] While in the reductive DPV a small back transition can be observed, this is absent on the CV time scale indicating that an electrochemical-chemical (EC) mechanism accompanies the oxidation of **1**. Due to the immediate reactivity of **1** with either ferrocene or decamethylferrocene we were not able to use an internal standard. Therefore, the given potentials are referenced only externally.[10d]

Subsequently, the chemical oxidation of **1** with NO[SbF$_6$] was carried out in toluene by mixing pre-cooled solutions of both at −78 °C (Scheme 2). Immediately, a pink coloration of the solution appeared which persists at −78 °C. Upon slowly increasing the temperature of the reaction mixture the color gradually transforms to a light-brown tinge at room temperature. The ^{1}H NMR spectrum of the crude reaction mixture shows the formation of **3**[SbF$_6$], a hydrogen abstracted product of the putative radical cation **2**. Most likely it is formed through the one-electron oxidation of **1** to radical cation **2** by NO[SbF$_6$] followed by hydrogen abstraction. From this reaction **3**[SbF$_6$] was isolated as light-brown crystalline solid with 68 % yield. The

interested in investigating the possibility of utilizing a CAAC **V** (Scheme 1) as one-electron reductant.

Herein, we report the one-electron donor property of CAAC **V** under the formation of radical cation **VI**, which was indicated by EPR spectroscopy, despite its limited stability and swift hydrogen[13] abstraction to **VII** (Scheme 1). To address this unprecedented one-electron donation of the CAAC **V**, it was utilized as reducing reagent for the synthesis of acyclic(amino)(aryl)carbene[14]-based Thiele and Chichibabin hydrocarbons,[15] a new class of Kekulé diradicaloids.[16] Notably, the latter shows an appreciable population of the triplet state at room temperature, as evidenced by both variable-temperature NMR and EPR spectroscopy.
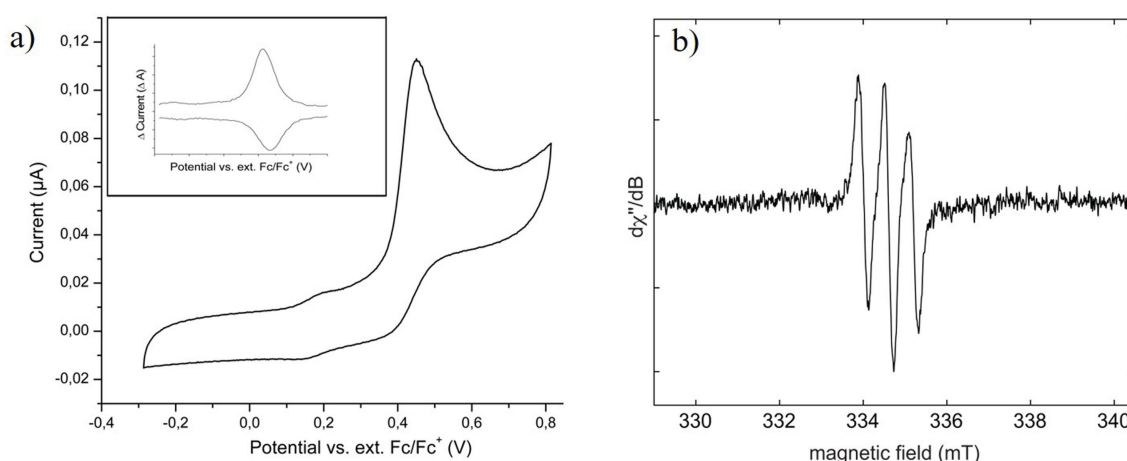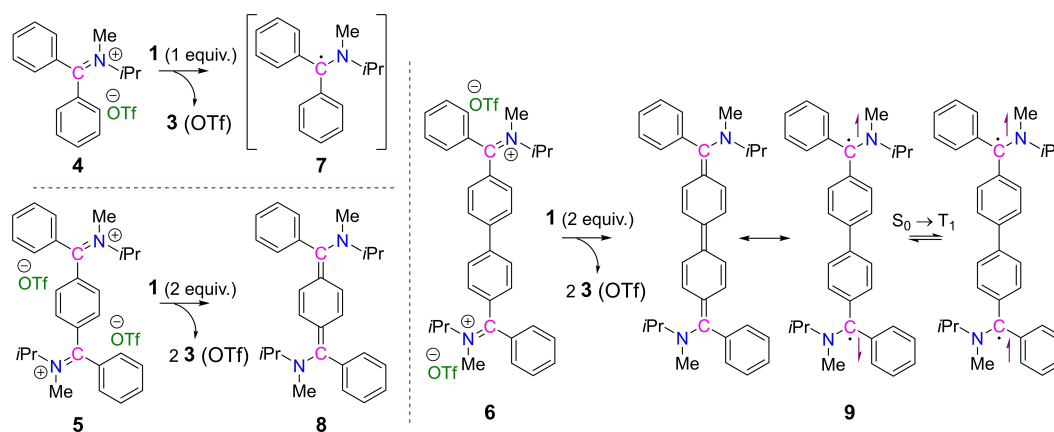

Figure 1. a) Cyclic voltammogram of **1** in THF (0.1 M Bu$_4$NPF$_6$) measured at a scan rate of 20 mV s^{-1}. Inset: Differential pulse voltammograms (DPV) of **1** in THF at a scan rate of 20 mV s^{-1} with 0.2 M Bu$_4$NPF$_6$). b) Experimental X-band EPR spectrum of a solution of **2** in toluene generated in situ at 200 K. The isotropic signal has a *g* value of 2.0043 and a ^{14}N hyperfine coupling of *a*(N) = 16.7 MHz (5.9 G).

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Scheme 3. Reactions of **1** with **4**, **5**, and **6**.

formation of **3**[SbF$_6$] was confirmed by solution state NMR spectroscopy and a solid-state single crystal X-ray diffraction study (Figure S50 in the Supporting Information).[18] A similar observation was also observed when we performed the oxidation using NO$_2$[BF$_4$]. During the course of the reaction, we did not observe any indication for the dimerization of **2** (dication of CAAC–CAAC dimer).[19] This is most likely due to the steric hindrance at the N-center. Also, we did not observe any reaction between **1** and **3**[SbF$_6$] which is in contrast with that of the N-iPr analogue.[20]

Using in-situ EPR spectroscopy, we found indication for the formation of a transient CAAC radical cation at low temperature. Monitoring the reaction at 200 K revealed the emergence of a triplet signal,[21] with a g value of 2.0043 and a nitrogen hyperfine coupling constant of $a(N) = 5.9$ G (Figure 1b), that only persisted at this temperature and readily disappeared at higher temperature.[22] The spin density plot of the optimized theoretical structure of **2** locates most of the unpaired electron on the carbenic carbon (Figure S56). The hyperfine coupling constant of $a(N)$ in **2** was calculated at various levels of theory.[17] However, in all these calculations, the hyperfine coupling constants for $a(N)$ are determined to be smaller than the experimentally observed value (the closest comp. $a(N) = 3.7$ G; exp. $a(N) = 5.9$ G; Table S9). Therefore, the anomaly observed between experimental and calculated hyperfine coupling constant $a(N)$ can be attributed to the accuracy of the computational methods.[23]

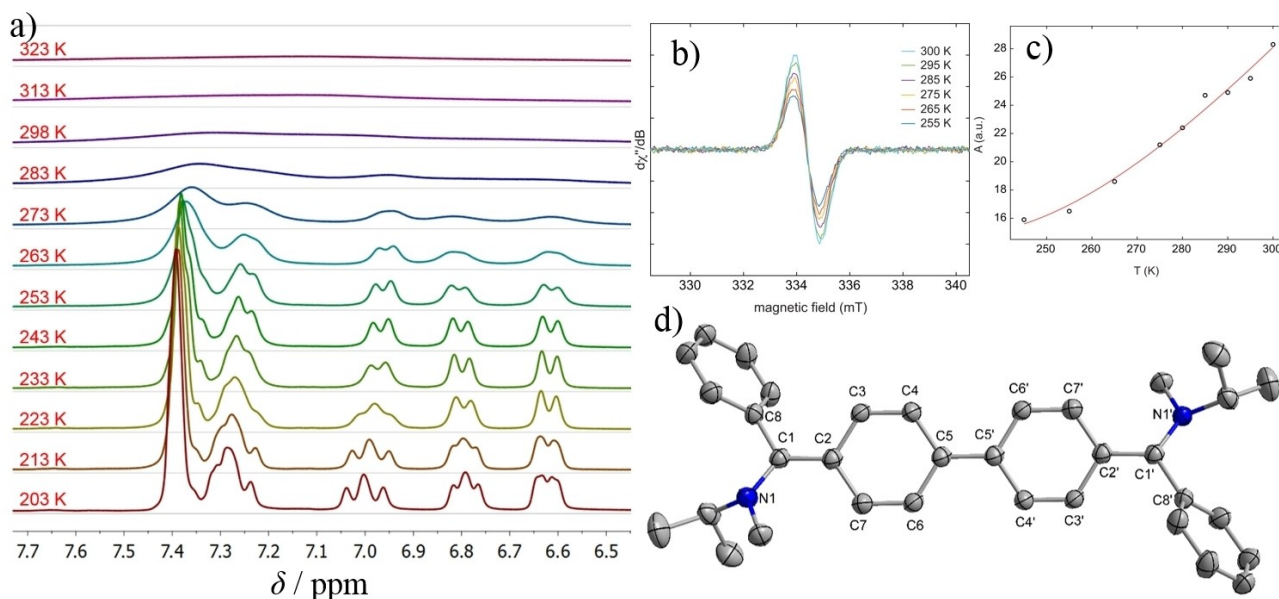Consequently, to study its utility as a reducing reagent CAAC **1** was reacted with amino(aryl)-based mono cation **4**, and p-phenylene and p,p'-biphenylene bridged dications **5** and **6** (Scheme 3).[17] The 1:1 reaction of **1** and **4** at −78 °C leads to the immediate appearance of an intense red color which steadily changes to light brown at room temperature. From the reaction mixture we were able to isolate **3**[OTf] in a 91% yield, which implies that CAAC **1** is first oxidized to the CAAC radical cation **2** and then forms the hydrogen abstracted product. The final product composition for the reduction of **4** was not conclusive. The ^{1}H NMR spectrum of the reaction mixture indicates the formation of an interactive mixture of products,

most plausibly the initial formation of neutral radical species **7** with a limited stability (the reduction of **4** also has been confirmed by the cyclic voltammetry study, which shows a reversible reduction wave: Figure 4, below). The in situ recorded EPR spectrum at 290 K (sample was prepared at 243 K and EPR spectrometer was precooled at about 250 K) shows a broad and unresolved signal (Figure S47). We tentatively assign the observed signal to the neutral radical species **7** or follow up decomposed products as we know that the corresponding CAAC-derived radical cation **2** is too reactive to be detected at more than 200 K and it shows a triplet signal.

The 1:2 reaction of **5** and **1** at −78 °C in THF immediately turns the solution red in color (Scheme 3). Crystallization in hexane after work up leads to pure product **8** (43%) as red colored compound which is well soluble in hexane, toluene, and THF. Compound **8** in hexane solution exhibits a strong absorption at λ_{max} $(\varepsilon) = 487$ nm (33 900 L mol^{-1} cm^{-1}) in the UV/Vis spectrum. In solution it is present as both syn and anti isomers in a 36:64 ratio. Quantum chemical calculations suggest that the syn isomer is more stable than the anti isomer by only 0.2 kcal mol^{-1}. In the crystalline solid state, only the anti isomer was observed by X-ray diffraction structural analysis (Figure S54).[18]

The 1:2 reaction of **6** and **1** at −78 °C in THF leads to the immediate appearance of a bluish green color (Scheme 3). Crystallization in hexane upon work up leads to pure product **9** (59%) as green colored compound which is soluble in hexane, toluene, and THF. The reactions of **1** with **5** and **6** lead to the formation of **8** and **9**, respectively, highlighting the CAAC as a potent organic reducing reagent.[24] Compound **9** in hexane exhibits a strong absorption in the UV/Vis spectrum at λ_{max} $(\varepsilon) = 608$ nm (75 000 L mol^{-1} cm^{-1}).

At room temperature the ^{1}H NMR spectrum of **9** exhibits broad resonances for the aromatic protons in [D$_8$]THF. This is an indication for a substantial population of the triplet state at room temperature. By lowering the temperature, the resonances for the aromatic protons gradually appear and at 203 K the resonances of the aromatic protons sharpen considerably (Figure 2a). In both solution and the solid state, **9** exhibits a

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Figure 2. a) Variable-temperature ^1H NMR spectra of **9** (selected region) in [D_8]THF. b) Variable-temperature X-band EPR spectra of **9** in THF between 255 and 300 K. C) plots of double-integral intensity (*A*) vs. *T*. The red line shows the fit to the Bleaney–Bowers equation (experimental parameters: microwave frequency = 9.38 GHz, microwave power = 0.2 mW, modulation amplitude = 0.5 G, modulation frequency = 100 kHz). d) Molecular structure of **9** with thermal ellipsoids at the 50% probability level. All H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: N1–C1 1.389(2), C1–C8 1.479(2), C1–C2 1.400(2), C2–C3 1.431(2), C3–C4 1.359(2), C4–C5 1.425(2), C5–C5' 1.419(21), N1–C1–C8 114.44(14).
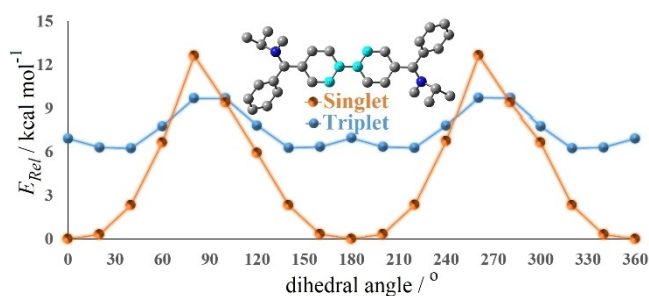
Figure 3. Energy scanning of the rotation of the C–C bond between the two phenyl rings of **9** for the broken-symmetry singlet (orange) and the triplet (blue) states at the UBP86-D3/Def2SVP level of theory.
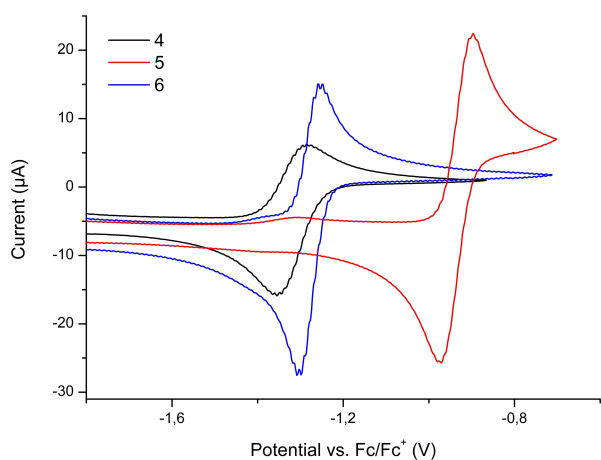
Figure 4. Cyclic voltammograms of **4**, **5**, and **6** in CH_3CN/0.1 M Bu_4NPF_6 measured at a GC working electrode.

broad unresolved EPR signal centered around $g = 2.0026$ which increases in intensity with increasing temperature (Figure 2b). Fitting of the temperature-dependent double-integral intensity to the Bleaney–Bowers model gives a singlet-triplet gap of $2J = -257$ cm^{-1} ($\Delta E_{ST} = -0.74$ kcal mol^{-1}), thus indicating a thermally excited triplet state. This is close to that of anionic boron- and carbon-based hetero-diradicaloids spanned by a *p*-phenylene bridge.[25]

The solid-state molecular structure of **9** (Figure 2d)[18] reveals that the C1–C2 bond length between the acyclic(amino)(aryl)carbene-scaffolds and the *p,p'*-biphenylene bridge as a π-conjugated spacer is 1.400(2) Å, thereby shorter than those in Chichibabin's hydrocarbon (1.415 Å).[25] The ∠N1-C1-C8 is 114.44(14)° which is more acute than that of the first crystalline acyclic(amino)(aryl)carbene (2,6-*t*Bu$_2$-C$_6$H$_3$-C(:)-N-(*i*Pr)Me) (121°).[13a] The dihedral angle between the planes involving acyclic(amino)(aryl)carbene-scaffolds (N1-C1-C8) and the adjacent phenyl spacer (C3-C2-C7) is 19.685(81)°. The arrangement of the two phenyl rings of the central *p,p'*-biphenylene bridge is coplanar. The bond length alternation (BLA) of **9** is 0.07 Å, that is, larger than in Chichibabin's hydrocarbon (0.05 Å).[26]

In order to obtain deeper insights into the diradical's character and energies, DFT studies were performed of the singlet and triplet states of **9**.[17] The adiabatic DFT calculations suggest that the singlet state has a lower energy than the triplet configuration by $\Delta E_{ST} = -6.9$ kcal mol^{-1} at the BP86-D3/Def2-SVP level of theory, whereas the experimentally derived EPR based ΔE_{ST} was determined to be -0.74 kcal mol^{-1}. Considering the effect of a torsional twist between two phenyl rings on the singlet-triplet gap, the energy alteration of singlet

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and triplet states was investigated by scanning of the corresponding dihedral angle.

We have also employed modredundant calculations for broken-symmetry singlet and triplet states (Figure 3). The calculations show that the torsional twist on the triplet state slightly affects the energy with up to ~ 3.4 kcal mol^{-1}. In the case of the singlet state, however, the influence is considerably high by at most ~ 12.5 kcal mol^{-1}. Therefore, the overestimation of the observed experimental and calculated ΔE_{ST} gap may stem from the rotation of the C–C bond between two phenyl rings and/or the accuracy of the computational method.

Due to the reactivity of **1** with either ferrocene or decamethylferrocene we were not able to exactly reference its redox potential. To investigate the redox potential of **1** indirectly, cyclic voltammograms of **4**, **5**, and **6** were recorded. The CVs exhibit reversible redox waves at $E_{1/2} = -1.32$ (**4**), -0.93 (**5**), and -1.28 (**6**) V versus external Fc/Fc$^+$, which we assigned to a one-electron reduction for **4** and to two-electron reductions for **5** and **6**, respectively (Figures 4 and S40). As **4**, **5**, and **6** can be reduced using **1**, it must have a redox potential $E_{1/2}$ of at least -1.3 V versus Fc/Fc$^+$.

Conclusion

In conclusion, a cyclic(alkyl)(amino)carbene (CAAC) acts as a potent one-electron reductant transforming to a radical cation in the process. The formation of the transient radical cation was indicated by EPR spectroscopy. The CAAC was then used as a reducing reagent for the synthesis of acyclic(amino)(aryl)carbene-based Thiele and Chichibabin hydrocarbons, a new class of Kekulé diradicaloids. Variable-temperature NMR and EPR spectroscopy studies show that the acyclic(amino)(aryl)carbene-based Chichibabin's hydrocarbon has an appreciable population of the triplet state at room temperature. The newly disclosed properties of CAACs might stimulate respective further exploration in new directions, such as single electron transfer processes[27] and use as n-type dopant/organic reductant.[28]

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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