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Organometallic Chemistry

Metallacyclobuta-(2,3)-diene: A Bidentate Ligand for Stream-line Synthesis of First Row Transition Metal Catalysts for Cyclic Polymerization of Phenylacetylene

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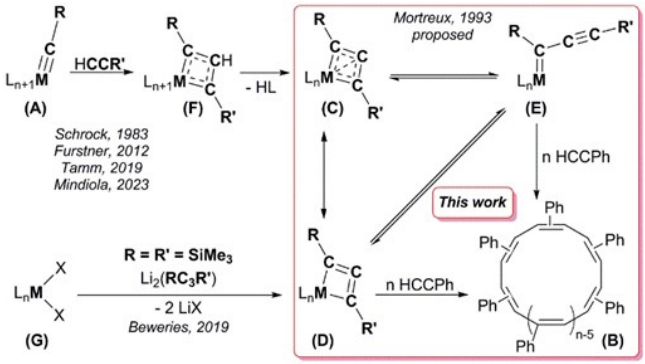
Abstract: Described here is a direct entry to two examples of 3d transition metal catalysts that are active for the cyclic polymerization of phenylacetylene, namely, [(BDI)M{κ²-*C*,*C*-($Me_3SiC_3SiMe_3$)}] (**2-M**) (BDI = [ArNC(CH_3)]$_2$$CH^-$, Ar = 2,6-^{i}$Pr_2C_6H_3$; **M** = **Ti, V**). Catalysts are prepared in one step by the treatment of [(BDI)MCl_2] (**1-M**, **M** = **Ti**, **V**) with 1,3-dilithioallene [Li_2($Me_3SiC_3SiMe_3$)]. Complexes **2-M** have been spectroscopically and structurally characterized and the polymers that are catalytically formed from phenylacetylene were verified to have a cyclic topology based on a combination of size-exclusion chromatography (SEC) and intrinsic viscosity studies. Two-electron oxidation of **2-V** with nitrous oxide (N_2O) cleanly yields a [V^V] alkylidene-alkynyl oxo complex [(BDI)V(=O)-{κ¹-*C*-(=C($SiMe_3$)CC($SiMe_3$))}] (**3**), which lends support for how this scaffold in **2-M** might be operating in the polymerization of the terminal alkyne. This work demonstrates how alkylidynes can be circumvented using 1,3-dianionic allene as a segue into M–C multiple bonds.

Linear polyalkynes are well known for their unique physical properties such as electrical conductivity,[1] gas permeability,[2] and surface properties.[3] More recently, investigations have focused on tailoring the topology of polymers by eliminating (via cyclization) the polymer chain ends to create cyclic polymers.[4–11] Cyclic polymers are synthesized via a variety of routes such as bi-[12] or uni-[13] molecular ring closures, ring opening metathesis polymerization (ROMP),[14] and ring expansion metathesis polymerization (REMP).[15–21] One attractive approach to synthesizing unsaturated cyclic polymers involves the use of homogeneous catalysts and alkyne monomers. This strategy has been pioneered by Veige and co-workers utilizing a high-valent [W^{VI}] catalyst and a variety of terminal alkynes.[22–29] Likewise, Maeda and co-workers have also reported cyclic polyalkynes of tolanes invoking Nb,[30] Ta,[31] and W[32] alkyne adducts. More recently, we have identified [V^V] alkylidynes (Scheme 1, **A**)[33–34] as pre-catalysts for the cyclic polymerization of phenylacetylene (*cyclic*-PPA, **B**).[35] Using a combination of experiment and theory we proposed and showed how a deprotiometallacyclobutadiene (dMCBD, Scheme 1, **C**), its resonance form, a metallacyclobuta-(2,3)-diene (bent-allene, Scheme 1, **D**), as well as a transient alkylidene-alkynyl (Scheme 1, **E**) could be likely species involved in the catalysis. Unfortunately, preparing the vanadium alkylidyne precursor required multiple steps such as alkylations, two oxidations, two α-hydrogen abstraction, and an anion exchange.[33–34] Prior to our work, seminal studies by Schrock,[36–42] followed by Weiss,[43] Fürstner,[44] and Tamm,[45] established dMCBD such as **C**, to be formed from a terminal alkyne and alkylidyne **A**, accompanied by H^+ loss from the metallacyclobutadiene (MCBD, Scheme 1,



Scheme 1. Previous work in the synthesis of metallacycles and their connection to the formation of cyclic-PPA.

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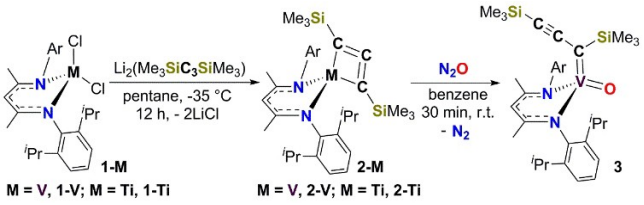
F). Although **C** forms polymers in the presence of terminal alkynes, the topology of the polymers produced was never established.[46] However, in 1993 Mortreux proposed that species **C** could rearrange to an active state alkylidene-alkynyl species (Scheme 1, **E**), which was speculated to promote metathesis polymerization of the terminal alkyne but with undefined topologies.[47]

Since metallacycles must be key intermediates in the formation of cyclic polyalkynes we decided to assemble complexes such as **D**, or its resonance **C**, directly while avoiding the need for synthetically cumbersome complexes, containing M–C multiple bonds such as **A** or **F**. This strategy is advantageous because it allows access to first row transition metal catalysts for which alkylidynes such as **A** are exceedingly rare.[33–34] Fortunately, recent studies of Reiß and Beweries[48–49] demonstrated how complexes such as **D** can be accessed in one-step using the trimethysilyl substituted 1,3-dilithioallene "$[Li_2(Me_3SiC_3SiMe_3)]$"[50–51] reagent and dihalide precursor **G**. Their work inspired us to investigate how metallacyclobuta-(2,3)-dienes engage in the formation of *cyclic*-PPA and how such as scaffold can be a precursor to a rare alkylidene-alkynyl motif. This study demonstrates how species **C**, **D** and **E** must be interconnected in the assembly of *cyclic*-PPA (**B**). More importantly, our work establishes a simple route to cyclic polymer catalysts using first row metals which avoids the cumbersome synthesis of alkylidyne precursors such as **A** (Scheme 1).

Accordingly, compounds $[(BDI)M\{\kappa^2\text{-}C,C\text{-}(Me_3SiC_3SiMe_3)\}]$ (**2-M**; **M** = **Ti**, **V**) were synthesized and purified in good yield (**Ti**, 75 %; **V**, 69 %) and in a single-step from readily available $[(BDI)MCl_2]$ (**1-M**)[52–53] (BDI = $[ArNC(CH_3)]_2CH^-$, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) and the respective 1,3-dilithioallene, $[Li_2(Me_3SiC_3SiMe_3)]$[50] (Scheme 2). Red **2-Ti** and red-orange **2-V** crystals can be obtained from a concentrated *n*-hexane solution stored at −35 °C for 24 h, and a single crystal X-ray diffraction study (sc-XRD) confirmed the assignment of a chelating metallacyclobuta-(2,3)-diene motif (Figure 1). According to their similar τ_4 values[54] of 0.77 and 0.84, respectively, both **2-Ti** and **2-V** exhibit distorted tetrahedral coordination geometries. Complex **2-V** displays similar M–C_α, C_α-C_β, and allene bond lengths to the previously isolated $[(BDI)V\{\kappa^2\text{-}C,C\text{-}(^tBu)C_3\text{-}(Mes)\}]$[35] but deviates slightly from **2-Ti** most likely as the result of their differing *d* electron counts despite having similar ionic radii ($[Ti^{III}]$: 81 pm; $[V^{III}]$: 78 pm).

The impact of d-electron counts can be correlated by comparing the metrical parameters to the d^0 complexes isolated by Beweries and co-workers ($[rac\text{-}(ebthi)Ti(\kappa^2\text{-}C,C\text{-}Me_3SiC_3SiMe_3)]$)[48] (Figure 2). As *d* electron count increases ($d^0 \rightarrow d^1 \rightarrow d^2$) the M–$C_\alpha$ bond length decreases (blue trace, Figure 2), and the C_α-C_β bond length increases (red trace, Figure 2), whereas the bent-allene bond angle decreases (black trace, Figure 2). Such a trend suggests that the bonding in these unsaturated metallacycles for the d^1 and d^2 systems might be more localized about the M–C linkage in comparison to the d^0 system. The more diffused electronic character about the M–C bond in our systems could tantalizingly imply a greater tendency for these systems to undergo change from **D** to forms **C** and even **E**. This is not unreasonable to propose since Reiß and Beweries have demonstrated this ligand to have non-innocence behavior and the possibility to resonate between **D** and **C**.[48–49]

Complexes **2-Ti** and **2-V** are paramagnetic with μ_{eff} = 1.68μ_B and 2.71μ_B, respectively (Evans method, 500 MHz, benzene-d_6, 300 K). These μ_{eff} values yield g = 1.94 for a spin-only S = 1/2 paramagnet for 3d^1 **2-Ti** and g = 1.92 for a spin-only S = 1 paramagnet for 3d^2 **2-V**. Half-integer spin **2-Ti** was subjected to X- and Q-band EPR spectral studies (Figure 3) in frozen solution revealing a narrow signal at *g*



Scheme 2. Synthesis of complexes **2-M** and trapping of the alkylidene-alkynyl **3** via oxidation with nitrous oxide (N_2O) (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$).

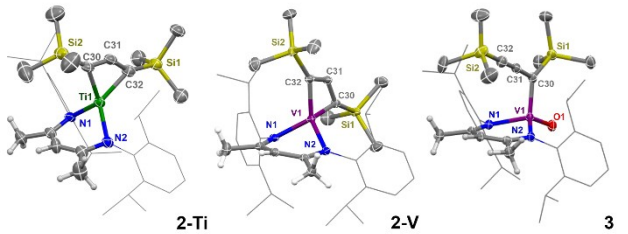


Figure 1. sc-XRD of **2-Ti**, **2-V** and **3** with ellipsoids shown at the 50 % probability level (except for the aryl fragments shown in a wireframe). H-atoms (except on the BDI ligand backbone) and residual solvent have been omitted for clarity.

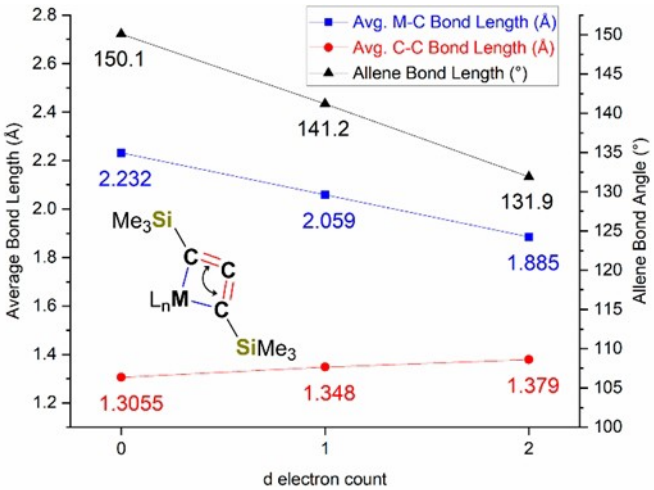


Figure 2. Average bond lengths M–C (red circles), C–C (blue rectangles), and C–C–C angle (black triangles) for 3dn metallacyclobuta-(2,3)-diene complexes (n = 0–2).

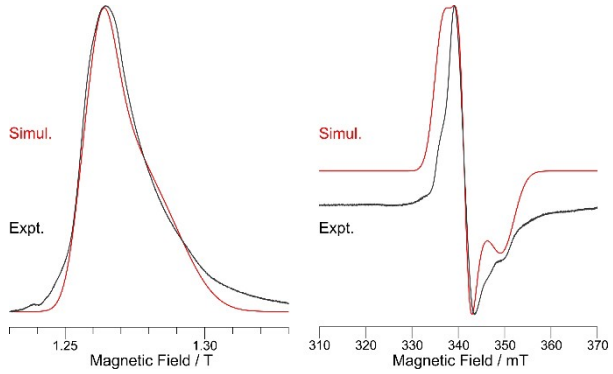
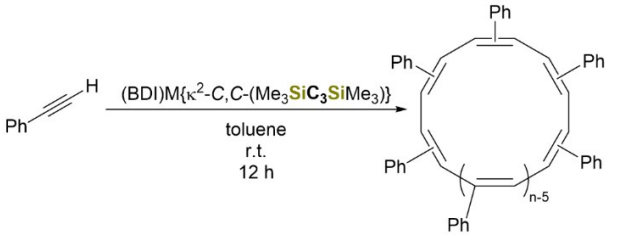


Figure 3. EPR spectra of complex 2-Ti (Q-band, left and X-band, right, black traces) with simulations (red traces).

≈1.96. Although the EPR simulations capture the essential features of the experimental spectra, the intensities of the individual components are not well reproduced. This difficulty at both Q- and especially X-band, where the narrower lines make the discrepancies more apparent, suggests that **2-Ti** does not exhibit a well-defined ***g***-tensor. It has been noted previously by Reiß and Beweries that metallacyclobuta-(2,3)-diene complexes do not exhibit a well-behaved electronic structure.[48] Perhaps, **2-Ti** is not a prototypical [Ti^{III}] complex due to contributions from various electronic configurations of the metallacyclobuta-(2,3)-diene.[48]

Given that Mortreux noted the activity of similar metallacycles such as **C** towards alkyne polymerization, we decided to explore the reactivity of these paramagnetic [V^{III}] and [Ti^{III}] complexes with a terminal alkyne such as phenylacetylene (PA). When an excess of PA was added to a stirring toluene solution of **2-M**, the reaction mixture became viscous within 12 h, and after precipitation the orange solid collected was confirmed to be *cyclic*-PPA on the basis of size-exclusion chromatography (SEC) (Figure S30, S35) and solution viscometry when compared to linear analogues of polyphenylacetylene (*linear*-PPA) (Figure S41), synthesized according to published procedures (Table 1).[55]

Table 1: Polymerization conditions and results.



M	[PA]:[Cat]	[PA] (M)	$M_{w,SEC}$ (g/mol)	Đ	T_g (°C)	Yield (%)[a]
V	100	1.0	30291	3.4	71	21
V	250	2.5	31499	3.6	75	14
V	500	5.0	47679	4.1	75	59
Ti	50	0.5	31720	3.6	74	16
Ti	100	1.0	38560	3.8	70	7
Ti	250	2.5	37554	3.5	71	7

[a] Determined based on the mass of polymer after work-up.

Cyclic polymers have a smaller hydrodynamic volume, compared to linear analogs of similar molecular weight. Therefore, SEC is used as a reliable method for distinguishing cyclic and linear polymers, as the cyclic polymer with a smaller hydrodynamic volume elutes later compared to the linear polymer with a larger hydrodynamic volume. Figure 4 (left) depicts the log (molar mass) versus elution time plot for *cyclic*-PPA (M_w = 30291 g/mol, $Đ$ = 3.4) derived from **2-V**, and *linear*-PPA (M_w = 45000 g/mol, $Đ$ = 6.4). At a given molar mass, *cyclic*-PPA elutes at a longer time compared to *linear*-PPA, revealing its compact nature and cyclic topology. Further, due to the smaller hydrodynamic volume, cyclic polymers inherently have smaller radii of gyration ($< R_g^2 >$). Theoretically, the $< R_g^2 >$ of a cyclic polymer is half of its linear counterpart. The center plot of Figure 4 highlights the smaller $< R_g^2 >$ of *cyclic*-PPA compared to *linear*-PPA over a wide range of molecular weights. Notably, the

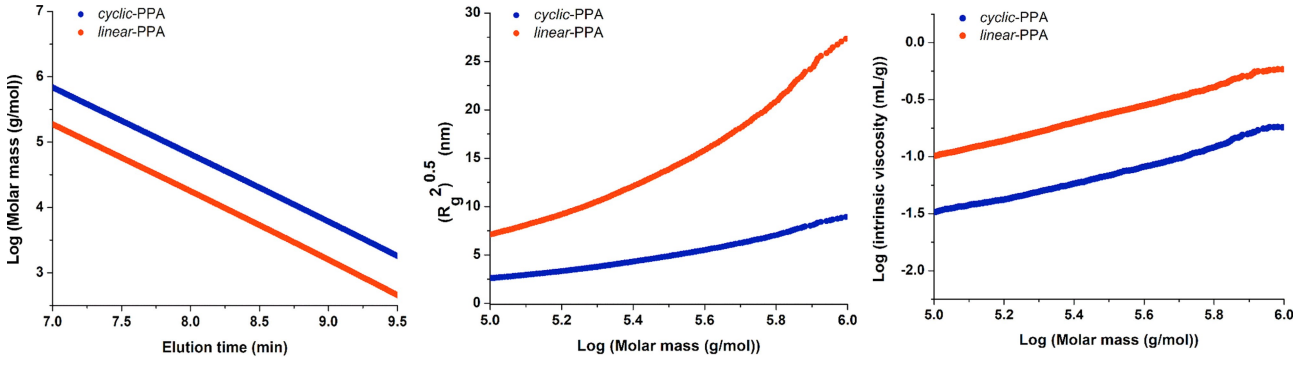


Figure 4. Left: Log(molar mass) versus elution time plot for *cyclic*-PPA (blue) and *linear*-PPA (orange) by SEC in THF at 35 °C. Center: Root mean square radius of gyration ($< R_g^2 >$) versus log (molar mass) plot for *cyclic*-PPA (blue) and *linear*-PPA (orange) by SEC in THF at 35 °C. Right. Mark-Houwink-Sakurada plot comparing intrinsic viscosity [η] over a range of molar masses for *cyclic*-PPA (blue) and *linear*-PPA (orange) by SEC in THF at 35 °C. *cyclic*-PPA samples catalyzed by **2-V** are shown herein, and data for *cyclic*-PPA samples catalyzed by **2-Ti** are in the Supporting Information (Figure S36–S38).

ratio of the mean square radius of gyration ($<R_g^2>_{cyclic\text{-}PPA}$ / $<R_g^2>_{linear\text{-}PPA}$) is 0.40, which is in close agreement with the theoretical value of 0.5. Cyclic polymers also have a lower intrinsic viscosity [η] than the linear analog, again due to the smaller hydrodynamic volume and compact nature. The right of Figure 4 depicts a Mark-Houwink-Sakurada (MHS) plot comparing the log (intrinsic viscosity) [η] of *cyclic*-PPA and *linear*-PPA as a function of molar mass. *cyclic*-PPA indeed exhibits lower intrinsic viscosities compared to *linear*-PPA over a wide range of molar mass, further confirming the cyclic topology of the polymer. The ratio of intrinsic viscosity ($[\eta]_{average,\ cyclic\text{-}PPA}$ /$[\eta]_{average,\ linear\text{-}PPA}$) was determined to be 0.41. Prior theoretical estimations suggest an intrinsic viscosity ratio of 0.58, under theta conditions ($a=0.5$).[56] The experimental results have reported ratios ranging from ~0.5 to ~0.8, for cyclic polymers made by ring-closing methods. This can be reasoned to the presence of linear impurities which could affect the [η] of cyclic polymer in solution. Previously, cyclic polymers made by ring-expansion methods exhibit ($[\eta]_{cyclic}$ /$[\eta]_{linear}$ ~0.4), which agrees with the results obtained in the present study.[57–58] Also, the MHS *a* value for *cyclic*-PPA and *linear*-PPA are 0.73 and 0.77, respectively, indicating that both the polymers behave as semi-flexible coils in THF under ambient conditions.[59] Furthermore, the bulk properties of the *cyclic*-PPA synthesized from **2-M** and *linear*-PPA were analyzed by differential scanning calorimetry (Figure S34, S39, and S40).

Since **2-M** must allow for binding of PA to then propagate the polymer, we reasoned that the metallacyclobuta-(2,3)-diene might rearrange to an alkylidene-alkynyl (**E**) and undergo alkylidene promoted polymerization of alkynes akin to what Mortreux proposed for the tungsten dMCBD species (vide supra).[47] Realizing that an alkyne is acting as a π-acceptor, we turned instead to an oxidant that would permanently trap the V center in a high-valent state. Accordingly, treatment of **2-V** with 1 atm of nitrous oxide in a pentane solution at room temperature yielded red colored [(BDI)V(=O){κ^1-*C*-(=C(SiMe$_3$)CC(SiMe$_3$))}] (**3**) in 64 % yield (Scheme 2). Diamagnetic complex **3** was characterized by multinuclear NMR spectroscopy in addition to sc-XRD, and Figure 1 shows its solid-state structure confirming a distorted tetrahedral geometry of the [V^V] ion, ($\tau_4=0.87$). Perhaps the most salient feature is that complex **3** contains an alkylidene-alkynyl ligand (V=C, 1.886(1) Å, C≡C, 1.222(2) Å). The pendant alkynyl motif was observed by IR at $\nu_{C\equiv C}=2012\ cm^{-1}$ (Figure S17), which is significantly red shifted in comparison to a previously reported chromium carbene-alkynyl complex, (OC)$_5$Cr(=C(NMe$_2$)CC(AuPPh$_3$) ($\nu_{1/2}=2321\ cm^{-1}$).[60] The V=C as well as V=O distance (1.601(1) Å) are comparable to those of the few known examples of [V^V] alkylidene-oxo derivatives.[61–64] It should be noted that [V^V] alkylidene-imido complexes are also active catalysts for ring-opening metathesis polymerization reactions so this strategy provides an independent route to vanadium alkylidenes.[65–67] Multidimensional and multinuclear NMR spectral studies were performed on complex **3** with the most salient feature being the broad alkylidene carbon resonating at 348 ppm in the ^{1}H-^{13}C{^{1}H} HMBC NMR spectrum (Figure S10). The latter feature is in agreement with the few characterized [V^V] alkylidene-oxo complexes, (PNP)V=CH^{t}Bu(=O) (335 ppm),[61] and (L)$_2$V(=O)(=CHSiMe$_3$)(Cl) (L=IMes, 332; PEt$_3$, 337–343 ppm).[63] Another salient feature is the ^{51}V NMR chemical shift of +809 ppm ($\Delta\nu_{1/2}=368$ Hz, Figure S11), which is far downfield when compared to the vanadium oxo alkylidene, (PNP)V=CH^{t}Bu(=O) (−58 ppm, $\Delta\nu_{1/2}=1304$ Hz).[61] The formation of complex **3** from oxidation of **2** provides strong credence that an unsaturated and strained metallacycle such as **C** could spring-open (e.g, retro-cyclo eliminate) to **E** to allow for an open coordination site for alkyne to bind and propagate the chain presumably via REMP. However, one cannot discard the possibility of alkyne insertion and expansion of the metallacycle. Complex **3** was also explored as a potential pre-catalyst for the formation of *cyclic*-PPA, however, no reaction was observed. This can be rationalized since the oxo ligand has blocked the coordination site that is necessary for monomer to bind in order to engage via [2+2] cycloaddition with the alkylidene moiety in **3**.

Salt metathesis of simple-to-prepare metal dihalides with a 1,3-dilithioallene allows for isolation of **2-M**. The latter paramagnetic systems have been extensively characterized and exhibited catalytic behavior for the polymerization of PA to form *cyclic*-PPA. Key to unravelling the mechanism of their polymerization, we demonstrate how a motif like **D** can be unveiled to reveal an alkylidene-alkynyl ligand, **E**, upon two-electron oxidation with nitrous oxide. Despite **2-M** not being highly active catalysts, potentially due to the bulky and electron withdrawing trimethylsilyl substituents on the metallacyclobuta-(2,3)-diene species, the most important conclusion is that our approach circumvents the need to prepare transition metal alkylidynes, thus opening the gate for first row transition metals to be streamline tested in cyclic polymerization catalysis.

Supporting Information

Supporting Information contains complete experimental details and characterization of new molecules including X-ray crystal structures **2-Ti** (2281446), **2-V** (2281445), and **3** (2281447). The authors have cited additional references within the Supporting Information.

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Conflict of Interest

J.B.R and D.J.M have filed a U.S. Provisional Application No. 63/488,610, March 6, 2023.

Data Availability Statement

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

Keywords: Alkylidene · Alkylidyne · Cyclic Polymer · Deprotiometallacyclobutadiene · Polymerization

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