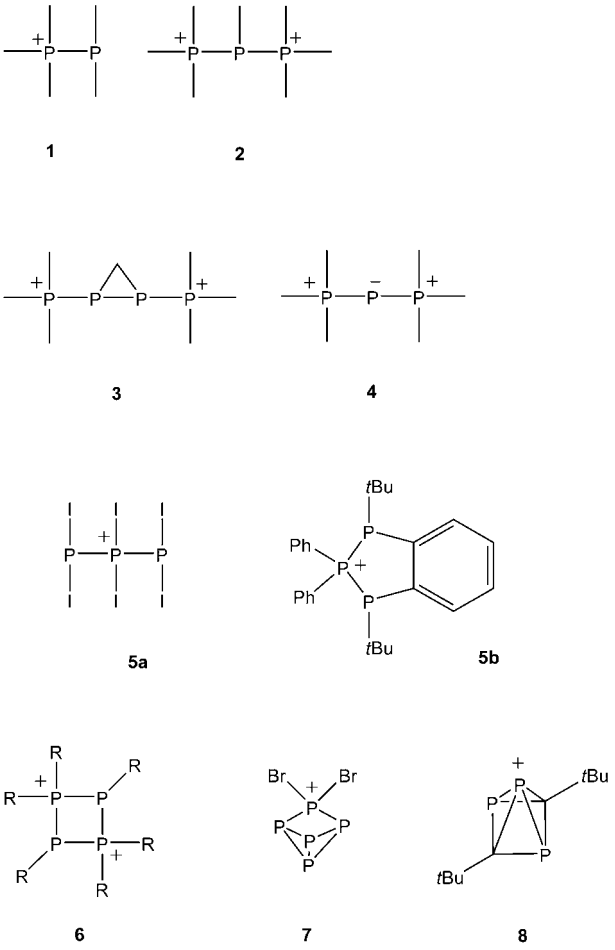

Scheme 1. Previously characterized polyphosphorus cations. ——= alkyl or aryl substituent; R = 2,6-$(OMe)_2C_6H_3$.

Phosphorus Chemistry

Facile Synthetic Methods for the Diversification of Catena-Polyphosphorus Cations**

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The propensity for phosphorus to form catenated compounds is evidenced by the extensive arrays of structurally characterized polyphosphines[1,2] and homopolyatomic anions reported.[3] In contrast, comprehensively characterized polyphosphorus cations are limited to phosphinophosphonium **1**,[4–9] phosphinodiphosphonium **2**,[10] diphosphiranodiphosphonium **3**,[11] and phosphidodiphosphonium **4**[12,13] ions (Scheme 1). Nevertheless, recent and unique examples of cations **5**,[7,14] **6**,[15] **7**,[8,14,16] and **8**[17] illustrate the potential for diversification and highlight catena-polyphosphorus cations as an underexplored avenue in phosphorus chemistry. In this context, we have exploited facile reactions of polyphosphines (di, tetra, and penta species) to prepare a series of new organosubstituted diphosphinophosphonium **9** and cyclotetraphosphinophosphonium cations **10**.

The ^{31}P NMR spectra for reaction mixtures of tetramethyldiphosphane or tetraphenyldiphosphane with Me_2PCl or Ph_2PCl in the presence of $Me_3SiOSO_2CF_3$ (TMSOTf)[18] show rapid, quantitative formation of the corresponding organo-substituted catena-diphosphanophosphonium cations **9a**, **9b**, **9c**, and **9f** (Scheme 2). Derivatives of **9** can be envisaged as diphosphine ligands on phosphenium Lewis acceptors (analogous to **1**, thus representing complexes of R_3P on R'_2P^+),[7] and are structural isomers of **4**.[12] Cation **9f** is a rearrangement product of **9d** or the product of Me_2P^+ insertion into the P–P bond of Ph_2P–PPh_2. The formation of derivative **9e** was not observed. The preferred formation of **9f** over **9d** and **9c** over **9e** is likely to be a result of the steric interactions between the substituents and the relative donor (PMe_2 versus PPh_2)/acceptor (PMe_2^+ versus PPh_2^+) properties of the PR_2 units.

An unusual eclipsed/staggered (C_s) conformation is observed for the cation of **9a**-OTf (OTf = trifluoromethanesulfonate) in the solid state (Figure 1). Retention of this nonsymmetric arrangement in solution is evidenced by the slight nonequivalence ($\Delta\delta < 0.1$ ppm, $\Delta J = 11$–35 Hz) of the terminal phosphorus centers in the ^{31}P NMR spectra of **9a**, **9b**, and **9f** at 193 K (Table 1; Figure 2 shows the ^{31}P NMR spectrum of **9b**-OTf as an example). The ^{31}P NMR spectra of all derivatives of **9** at RT show broad, poorly defined triplets and doublets, thus indicating dynamic behavior that may enable rearrangement of **9d** to **9f** by dissociation to Ph_2P–PMe_2 and Ph_2P^+ (Scheme 2).

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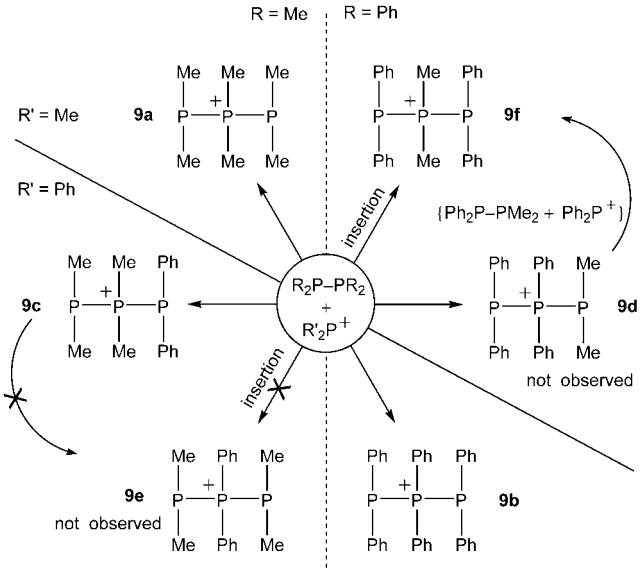


Scheme 2. Derivatives of **9** generated from the reaction of diphosphine ligands with phosphenium Lewis acceptors in the presence of R'_2PCl, TMSOTf, and $R_2P{-}PR_2$.

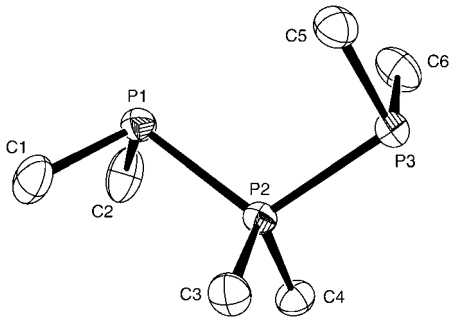


Figure 1. The solid-state structure of the cation **9a**, with thermal ellipsoids at the 50% probability level (hydrogen atoms and OTf anion are omitted). P1–P2 221.60(6), P2–P3 218.83(6) pm; P-P-P 111.56(3)°.

The ^{31}P NMR spectra for equimolar mixtures of R_2PCl and TMSOTf with $(PhP)_4$ or $(PhP)_5$ [Eqs. (1) and (2);

$$(PhP)_4 + R_2PCl + TMSOTf \rightarrow \mathbf{10a,b}\text{-OTf} + TMSCl \quad (1)$$

$$4\,(PhP)_5 + 5\,R_2PCl + 5\,TMSOTf \rightarrow 5\,\mathbf{10a,b}\text{-OTf} + 5\,TMSCl \quad (2)$$

TMS = trimethylsilyl; **10a**: R = R′Ph, **10b**: R = R′ = Me] demonstrate quantitative formation of the corresponding cyclotetraphosphanophosphonium triflate salts **10a**-OTf or **10b**-OTf (Figure 3). The solid-state structure of the cation **10a** is shown in Figure 4. Although complicated, the ^{31}P NMR solution spectra for the derivatives of **10** exhibit a low-field tripletlike signal that is assigned to a phosphonium center and is distinct from a multiplet that corresponds to the four phosphine centers (Figure 3a, b). The exclusive formation of **10a** and **10b** from either $(PhP)_4$ or $(PhP)_5$ demonstrates a thermodynamic preference for the five-membered framework over the hexaphosphorus or pentaphosphorus alternatives **11** and **12** (Scheme 3) and is consistent with the prominence of the cyclopentaphosphorus unit in Hittorf's phosphorus,[19] polyphosphines, and polyphosphorus anions.[3]

Pentaphosphorus cations of type **10** were first proposed on the basis of elemental analysis data for the alkylation products of cyclopentaphosphines.[20,21] This prompted us to exploit the methylation of penta-, tetra-, and diphosphines as an alternative and facile route to phosphinophosphonium cations. New derivatives of **1** were readily observed by ^{31}P NMR spectroscopic analysis as quantitative products (see, **1a**-OTf

Table 1: ^{31}P NMR data for polyphosphines and derivatives of **1**, **2**, **4**, **5**, **9**, and **10**. P_A refers to the phosphonium center(s) and P_B refers to the phosphine center(s) (phosphide center for **4**). New compounds were observed in CH_2Cl_2, and salts contain OTf anions unless otherwise stated.

Compound	$^{31}P_A$ [δ]	$^{31}P_B$ [δ]	$J_{P,P}$ [Hz]	Ref.
$(PhP)_5$		−3[b]	[b]	[22]
$(PhP)_4$		−48	N/A	[24]
$Ph_2P{-}PPh_2$		−14	N/A	[25]
1a $(Me_3P{-}PMe_2)^+$	18	−60	275	[i]
1b $(MePh_2P{-}PPh_2)^+$	15	−18	375	[i]
1c $(Ph_3P{-}PPh_2)^+$	15	−10	340	[7]
1d $(Me_3P{-}PPh_2)^+$	15	−23	289	[7]
1e $(I_3P{-}PI_2)$ (A)[a]	−156	126	[c]	[8]
2 $(Ph_3P{-}PH{-}PPh_3)(AlCl_4)_2$	23	−120	286	[10]
4 $(Ph_3P{-}P{-}PPh_3)(AlCl_4)$	30	−174	502	[12]
5a $(I_2P{-}PI_2{-}PI_2)$ (A)[a]	−5	89	386	[14]
9a $(Me_2P{-}PMe_2{-}PMe_2)^+$[d]	12	−58[f]	303, 292	[i]
9b $(Ph_2P{-}PPh_2{-}PPh_2)^+$[e]	18	−22[f]	365, 335	[i]
9c $(Me_2P{-}PMe_2{-}PPh_2)^+$[e]	8	−52[g], −28[h]	331[g], 296[h]	[i]
9f $(Ph_2P{-}PMe_2{-}PPh_2)^+$[d]	5	−20	357, 313	[i]
10a $(Ph_6P_5)^+$	22[b]	−38[b]	[b]	[i]
10b $(Ph_4Me_2P_5)^+$	26[b]	−29[b]	[b]	[i]
10c $(Ph_5MeP_5)^+$	21[b]	−30[b]	[b]	[i]

[a] [A] = $[((F_3C)_3CO)_3AlFAl(OC(CF_3)_3)_3]$; measured at 183 K. [b] Complex multiplet. [c] Not observed at 183 K. [d] Measured at 220 K, $CDCl_3$. [e] Measured at 193 K. [f] Two signals with $\Delta\delta < 0.1$ ppm. [g] PPh_2 group. [h] PMe_2 group. [i] This work.

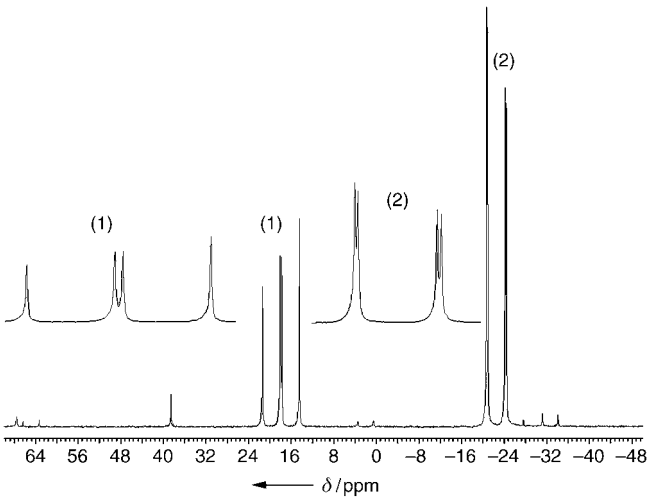


Figure 2. The ^{31}P NMR spectrum for the reaction mixture of Ph_4P_2, Ph_2PCl, and TMSOTf (formation of **9b**-OTf) at 193 K. Signal (1) corresponds to the central P atom, which is coupled to the two nonequivalent terminal P centers responsible for the two doublets labeled (2).

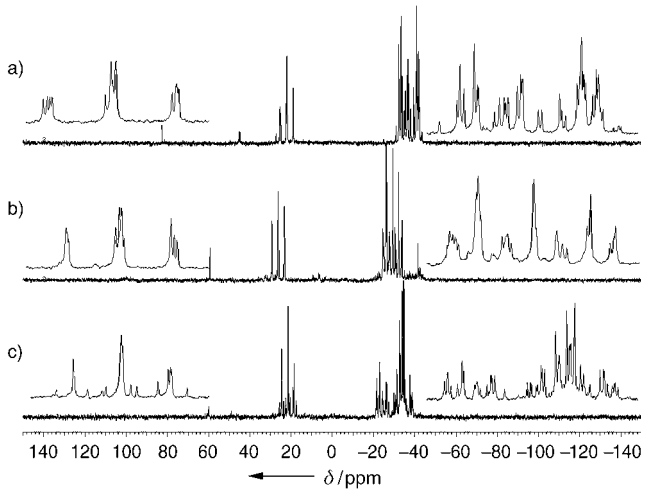


Figure 3. The ^{31}P NMR spectra (RT) for the reaction mixtures of: a) $(PhP)_5$, Ph_2PCl, and TMSOTf (quantitative formation of **10a**-OTf); b) $(PhP)_5$, Me_2PCl, and TMSOTf (quantitative formation of **10b**-OTf); c) $(PhP)_5$ and MeOTf (quantitative formation of **10c**-OTf; see Experimental Section for stoichiometry). Essentially identical spectra were observed for analogous reactions of $(PhP)_4$.

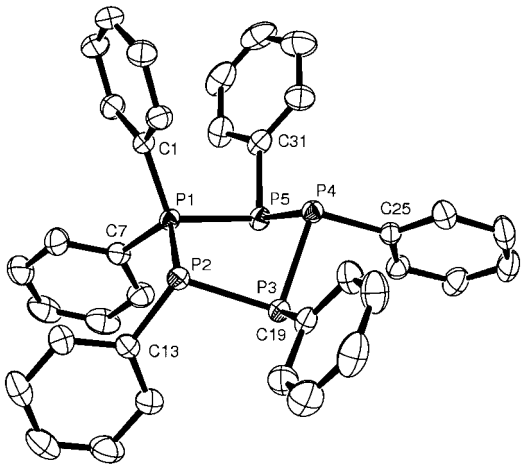
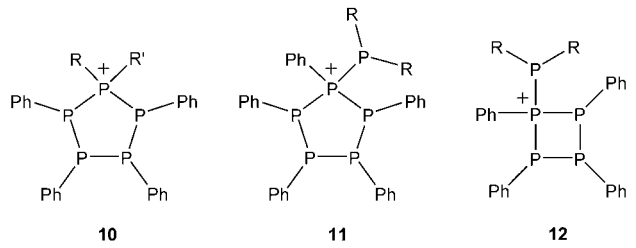


Figure 4. The solid-state structure of the cation **10a**, with thermal ellipsoids at the 50% probability level (hydrogen atoms and OTf anion are omitted). P–P bond lengths range from 220.72(6) to 223.92(6) pm, P-P-P angles range from 89.56(2) to 96.52(2)°.



Scheme 3. Cyclotetraphosphinophosphonium triflate salts **10** and the hexaphosphorus or pentaphosphorus alternatives **11** and **12**. **10a**: R = R′ = Ph, **10b**: R = R′ = Me, **10c**: R = Me, R′ = Ph; **11**,**12**: R = Me or Ph.

and **1b**-OTf [Eq. (3)] compared to $(Ph_3P–PPh_2)$OTf (**1c**-OTf) and $(Me_3P–PPh_2)$OTf (**1d**-OTf);[7] Table 1) in equimolar

(3)

1a R = Me
b R = Ph

mixtures of Me_2PPMe_2 or Ph_2PPPh_2 with methyltrifluoromethanesulfonate (MeOTf). Both the cyclophosphines $(PhP)_4$ and $(PhP)_5$ react rapidly with an excess of MeOTf according to Equations (4) and (5), respectively, to give **10c**, as shown by

$$5\,(PhP)_4 + 4\,TMSOTf \rightarrow 4\,\mathbf{10c}\text{-OTf} \quad (4)$$

$$(PhP)_5 + 4\,MeOTf \rightarrow \mathbf{10c}\text{-OTf} \quad (5)$$

^{31}P NMR spectroscopic analysis of the reaction mixtures (Figure 3c), which further highlights the thermodynamic preference for the framework of **10**.

In summary, facile association of diphosphines with phosphenium ions represents a general and versatile synthetic method for new organodiphosphinophosphonium cations **9**, which are isomers of phosphidodiphosphonium **4**. Similar reactions involving cyclotetra- or cyclopentaphosphines result in the exclusive formation of cyclotetraphosphinophosphonium cations **10**. We anticipate further application of these synthetic methods will result in the efficient and diverse development of catena-polyphosphorus cations.

Experimental Section

All operations were carried out in an N_2 atmosphere. Caution: Phosphine reagents have a pungent odor and $Me_2P–PMe_2$ is pyrophoric. The ^{31}P NMR data presented in Table 1 were obtained within 40 min of mixing the colorless reaction mixtures and show quantitative formation of: **1a**-OTf and **1b**-OTf from equimolar quantities of MeOTf (0.10 mmol) and $R_2P–PR_2$ (0.10 mmol); **9f**-OTf from PMe_2Cl (0.37 mmol), TMSOTf (0.44 mmol), and $Ph_2P–PPh_2$ (0.37 mmol); **10c**-OTf from MeOTf (0.46 mmol) and $(PPh)_5$[26] (0.093 mmol). **9c**-OTf was observed in high yield from Ph_2PCl (0.093 mmol), TMSOTf (0.11 mmol), and Me_2PPMe_2 (0.093 mmol) with **9a**-OTf as a minor product. Spectra for other derivatives were obtained from the samples described below. Spectra for reactions of $(PPh)_4$[24] with PPh_2Cl/TMSOTf, PMe_2Cl/TMSOTf, or MeOTf were obtained from samples containing tetraphosphine as the limiting reagent.

9a-OTf: Me_2PCl (0.37 mmol) was added to TMSOTf (0.44 mmol) in CH_2Cl_2 (6 mL) followed by $Me_2P–PMe_2$ (0.37 mmol). Vapor diffusion of diethyl ether into the reaction mixture at −28 °C caused crystallization; yield = 0.076 g (0.23 mmol, 62%). Decomp. 44–65 °C; elemental analysis (%) for $C_7H_{18}F_3O_3P_3S$: C 25.3, H 5.5; found: C 25.2, H 5.2; ^{1}H NMR (250.1 MHz, $CDCl_3$, 220 K): δ = 2.0 (d, J(P,H) = 13 Hz, 1H), 1.5 ppm (d, J(P,H) = 18 Hz, 2H); FTIR (nujol (ranked intensities)): $\tilde{\nu}$ = 1314 (8), 1302 (7), 1260 (1), 1224 (3), 1154 (4), 1031 (2), 977 (11), 934 (12), 892 (6), 638 (5), 573 (10), 517 (9) cm^{-1}.

9b-OTf: Ph_2PCl (0.28 mmol) was added to TMSOTf (0.33 mmol) in C_6H_5F (1 mL) followed by $Ph_2P–PPh_2$ (0.28 mmol) in C_6H_5F (1 mL). Slow diffusion of diethyl ether into the filtered solution at −28 °C afforded a white solid, which was washed with diethyl ether

(2 × 3 mL); yield = 0.127 g (0.18 mmol, 64 %). M.p. 138–142 °C; elemental analysis (%) calcd for $C_{37}H_{30}F_3O_3P_3S$: C 63.1, H 4.3; found: C 62.2, H 4.2; FTIR (nujol, (ranked intensities)): $\tilde{\nu}$ = 1264 (1), 1223 (2), 1149 (7), 1090 (11), 1030 (6), 742 (4), 691 (3), 636 (5), 570 (10), 515 (9), 450 (8) cm^{-1}.

10a-OTf: Ph_2PCl (0.25 mmol) was added to TMSOTf (0.30 mmol) in CH_2Cl_2 (2 mL) followed by $(PhP)_5$[26] (0.185 mmol) in CH_2Cl_2 (2 mL). The solvent was removed in vacuo and the solid washed with hexane (2 × 4 mL); yield = 0.123 g (0.16 mmol, 87 %). Decomp. 65–75 °C; elemental analysis (%) calcd for $C_{37}H_{30}F_3O_3P_5S$: C 58.0, H 3.9, P 20.2; found: C 57.4, H 3.9, P 20.4; ^{1}H NMR (250.1 MHz, $CDCl_3$, 298 K): complex multiplets δ = 7.2–7.9 ppm; FTIR (nujol (ranked intensities)): $\tilde{\nu}$ = 1312 (11), 1263 (1), 1146 (6), 1093 (8), 1029 (2), 997 (9), 843 (7), 740 (3), 687 (5), 635 (4), 570 (12), 517 (10) cm^{-1}.

10b-OTf: Me_2PCl (0.185 mmol) was added to TMSOTf (0.22 mmol) in CH_2Cl_2 (2 mL), and this solution was added to $(PhP)_5$[26] (0.093 mmol). Filtration and slow diffusion of diethyl ether vapor into the solution at −28 °C caused precipitation; yield = 0.027 g (0.042 mmol, 45 %). M.p. 142–145 °C; elemental analysis (%) calcd for $C_{27}H_{26}F_3O_3P_5S$: C 50.5, H 4.1; found: C 49.4, H 3.6; ^{1}H NMR (250.1 MHz, $CDCl_3$, 298 K): complex multiplets δ = 1.8–1.9 ppm, 7.4–7.9 ppm; FTIR (nujol (ranked intensities)): $\tilde{\nu}$ = 1304 (8), 1288 (1), 1247 (2), 1150 (7), 1032 (3), 958 (10), 918 (9), 733 (4), 691 (5), 638 (6), 572 (13), 516 (12), 465 (11) cm^{-1}.

X-ray crystallography: Data collection on Bruker AXS P4/SMART 1000 diffractometer by using ω and θ scans with a width of 0.3° and 10 s (**9a**-OTf) or 30 s (**10a**-OTf) exposure times with a detector distance of 5 cm. The data were reduced (SAINT)[27] and corrected for absorption (SADABS).[28] Structures were solved by direct methods and refined by full-matrix least squares on F^2-(SHELXL).[29] All nonhydrogen atoms were refined anisotropically. **9a**-OTf: $C_7H_{18}F_3O_3P_3S$; colorless, irregular, crystal size 0.60 × 0.15 × 0.15 mm; monoclinic, space group $P2_1/c$, a = 11.9395(8), b = 11.3475(7), c = 12.3165(8) pm, β = 115.818(1)°, V = 1502.1(2), Z = 4, μ = 0.561 mm^{-1}; $\lambda(Mo_{K\alpha})$ = 0.71073 Å, T = 173 K, $2\theta_{max}$ = 53.5°, collected (independent) reflections = 10152 (3362), R_{int} = 0.0210; 226 refined parameters, R_1 = 0.0323, wR_2 = 0.0796 for reflections with $I > 2\sigma(I)$, max/min residual electron density = 0.543/−0.455 e $Å^{-3}$. **10a**-OTf: $C_{37}H_{30}F_3O_3P_5S$; colorless rod, crystal size 0.60 × 0.20 × 0.10 mm; monoclinic, space group $P2_1/c$, a = 10.6004(6), b = 16.7110(8), c = 20.601(1) pm, β = 92.255(1)°, V = 3550.8(3), Z = 4, μ = 0.369 mm^{-1}; $\lambda(Mo_{K\alpha})$ = 0.71073 Å, T = 198 K, $2\theta_{max}$ = 53.4°, collected (independent) reflections = 23629 (7915), R_{int} = 0.0232; 562 refined parameters, R_1 = 0.0343, wR_2 = 0.0861 for reflections with $I > 2\sigma(I)$, max/min residual electron density = 0.432/−0.421 e $Å^{-3}$.

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