A Novel Type of Alkynylgold(I) Complex. Crystal and Molecular Structures of PPN[Au(Ar)(C≡CH)] [Ar = C_6F_5, $C_6H_2(NO_2)_3$-2,4,6]

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*Summary: Complexes of the type PPN[Au(acac)(Ar)] [PPN = $(Ph_3P)_2N$, acac = acetylacetonate], obtained in solution from Tl(acac) and the corresponding PPN[Au(Ar)Cl] derivatives after removal of TlCl, react in situ with ethyne to give a new type of ethynylgold(I) complex, PPN[Au(Ar)(C≡CH)] [Ar = C_6F_5 (**1**), $C_6H_4NO_2$-2 (**2**), $C_6H_2(NO_2)_3$-2,4,6 (**3**)]. The crystal structures of **1** and **3** have been determined.*

Introduction

The preference of gold(I) for linear dicoordination, together with the linearity of the C≡C bond in alkynyl ligands, makes alkynylgold(I) complexes attractive candidates for the design of linear-chain metal-containing polymers with extended electronic conjugation along the backbone.[1] The rapidly growing interest in alkynylgold(I) complexes is associated with the expectation that these electronically flexible rigid-rod polymers might exhibit interesting properties either difficult or impossible to achieve with conventional organic polymers. Among the many alkynylgold(I) complexes described, some show liquid crystalline properties[2] or nonlinear-optical behavior.[3] In addition, some alkynylgold(I) derivatives belong to a new class of luminophores with interesting photophysical and photochemical properties.[4]

Although a few of the reported alkynylgold(I) complexes are anionic or cationic,[5] most of them are neutral and the majority correspond to the types [Au(C≡CR)(L)],[4a,5f,g,6] $[(AuL)_2(\mu\text{-}C{\equiv}C)]$[5g,7] $[(AuL)_2(\mu\text{-}C{\equiv}C{-}R{-}C{\equiv}C)]$,[1d] $[(AuL)_3(\mu\text{-}R\{C{\equiv}C\}_3)]$,[8] or $[\{Au(C{\equiv}CR)\}_2(\mu\text{-}L{-}L)]$ (L = tertiary phosphine, L−L = diphosphine).[1d,4b,9] A limited number of alkynylgold(I) complexes with isocyanide,[1a,b,e,2,5g] amine,[5g,6a,10] carbene,[5g] or ylide ligands[11] have also been reported, as have polymeric compounds $[Au_2C_2]_n$,[12] $[RC{\equiv}CAu]_n$,[6a] or $[AuC{\equiv}CR'C{\equiv}CAu]_n$.[1a] In most cases, R or R′ is an aryl group, but a few examples have R = Me, Et,[6b,13] CF_3,[1e,6b,f] Bu^t,[5g,6a,9e,11] Me_3Si,[5g] R″CHX (X = OH, Cl, Br),[5g,14] CO_2Me,[6g,13] or $MeOCH_2$.[15]

Despite the great number of reported alkynylgold(I) complexes, the ethynyl derivatives are very scarce.[6g,16] In this paper, we report new ethynylgold(I) complexes $[Au(Ar)(C{\equiv}CH)]^-$ (Ar = C_6F_5, $C_6H_4NO_2$-2, $C_6H_2(NO_2)_3$-2,4,6) representing the first mixed arylalkynylgold complexes. We also describe the first crystal structures of ethynylgold complexes.

Experimental Section

IR spectroscopy, elemental analyses, conductance measurements in acetone solution, melting point determinations, and NMR spectroscopy were carried out as described elsewhere.[16c] Complexes PPN[Au(Ar)Cl] (Ar = C_6F_5,[17] $C_6H_4NO_2$-2,[18] and $C_6H_2(NO_2)_3$-2,4,6[19] were prepared following the methods reported in the literature. The NMR spectra were recorded in

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$CDCl_3$ at room temperature. Chemical shifts are referenced to TMS [^{1}H, ^{13}C{^{1}H}], H_3PO_4 [^{31}P{^{1}H}], or $CFCl_3$ (^{19}F). DEPT experiments allowed us to assign the resonances from the carbon nuclei attached to the gold atom. Some spectroscopic data of the PPN cation, which are not listed below, are as follows: NMR (δ), ^{1}H, 7.4−7.7 (m, 30H); ^{13}C{^{1}H}, 127 (m, C_{ipso}), 129.5 (m, C_{ortho}), 132 (m, C_{meta}), 134 (m, C_{para}) ppm; ^{31}P{^{1}H}, 20.9 (s) ppm; IR spectra, 1580 (m), 1320−1220 (s, br), 545 (s), 525 (s), and 490 (s) cm^{-1}.

Syntheses of PPN[Au(Ar)(C≡CH)] [Ar = C_6F_5 (1), $C_6H_4NO_2$-2 (2), $C_6H_2(NO_2)_3$-2,4,6 (3)]. Tl(acac) (0.2−0.9 mmol) was added to a solution of PPN[Au(Ar)Cl] (0.15−0.67 mmol) in CH_2Cl_2 (20 mL) (**1**) or in acetone (20 mL) (**2**, **3**), and the resulting mixture was stirred for 40 min. The resulting suspension was filtered through Celite, C_2H_2 was bubbled through the solution for 30 min (**1**) or 2 h (**2**, **3**) and it was then filtered through anhydrous $MgSO_4$. The filtrate was concentrated to ca. 1 mL, and Et_2O (20 mL) was added to precipitate **1** as a white solid, and **2** or **3** as yellow solids.

1: yield, 80%. Mp: 148 °C. Anal. Calcd for $C_{44}H_{31}AuF_5NP_2$: C, 56.97; H, 3.39; N, 1.51. Found: C, 56.48; H, 3.79; N, 1.42. Λ_M: 100 Ω^{-1} cm^2 mol^{-1}. NMR (300 MHz, δ): ^{1}H, 1.59 (s, ≡CH, 1H); ^{13}C{^{1}H}, 65.77 (s, ≡CH), 88.22 (s, AuC≡); ^{19}F, −164.90 (m, 2F, *m*-F), −163.64 (m, 1F, *p*-F), −114.99 (m, 2F, *o*-F). Mass spectrum (FAB, negative ion mode): *m*/*z* (% abundance) 389 (M^-, 15.1), 532 ($[Au(C_6F_5)_2]^-$, 100), 752 ($[Au_2(C_6F_5)_2C_2]^{2-}$, 16.9). IR (cm^{-1}): ν(≡C−H), 3268 (w); ν(C≡C), 1970 (m); $\nu(C_6F_5)$, 1498, 948, 788.

2: yield, 88%. Mp: 168 °C. Anal. Calcd for $C_{44}H_{35}AuN_2O_2P_2$: C, 59.87; H, 4.00; N, 3.17. Found: C, 59.61; H, 3.94; N, 3.07. Λ_M: 106 Ω^{-1} cm^2 mol^{-1}. NMR (200 MHz, δ): ^{1}H, 1.52 (s, ≡CH, 1H), 6.91 (m, C_6H_4, 1H), 7.20 (m, C_6H_4, 1H), 7.42−7.68 (m, PPN + C_6H_4, 31H), 7.77 (m, C_6H_4, 1H); ^{13}C{^{1}H}, 89.11 (s, ≡CH), 122.56 (s, C_6H_4), 123.17 (s, C_6H_4), 127.10 (s, Au*C*CH), 130.56 (s, C_6H_4), 142.94 (s, C_6H_4), 159.14 (s, CAu), 169.11 (s, CNO_2). IR (cm^{-1}): ν(≡C−H), 3284 (w); ν(C≡C), 1968 (w); $\nu_{asym}(NO_2)$, 1504 (m).

3: yield, 56%. Mp: 170 °C (dec). Anal. Calcd for $C_{44}H_{33}AuN_4O_6P_2$: C, 54.33; H, 3.42; N, 5.76. Found: C, 54.26; H, 3.38; N, 5.56. Λ_M: 88 Ω^{-1} cm^2 mol^{-1}. NMR (200 MHz): ^{1}H, 1.57 (s, ≡CH, 1H), 8.66 (s, C_6H_2, 2H); ^{13}C{^{1}H}, 90.05 (s, ≡CH), 120.17 (s, C_6H_2), 121.51 (s, AuC≡), 143.96 (s, C_6H_2), 160.46 (s, C_6H_2). IR (cm^{-1}): ν(≡C−H), 3259 (w); ν(C≡C), 1962 (w); $\nu_{asim}(NO_2)$, 1530 (s), 1514 (s).

X-ray Crystallographic Analysis of 1 and 3. Crystal data and refinement details are presented in Table 1. Crystals were mounted on glass fibers in inert oil and transferred to the cold gas stream (−100 °C) of a Siemens P4 diffractometer. Data were registered to $2\theta_{max}$ 50° in ω-scan mode using Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were applied on the basis of ψ-scans. Structures were solved by the heavy-atom method and refined anisotropically on F^2 (program SHELXL-93, G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included with a riding model (exception: the acetylenic H of **1** was located and refined freely). A system of restraints (to local ring symmetry and light atom displacement parameters) was employed to ensure refinement stability.

Table 1. Crystal Data and Structure Refinement for 1 and 3

	1	**3**
empirical formula	$C_{47}H_{37}AuF_5NOP_2$	$C_{44}H_{33}AuN_4O_6P_2$
fw	985.68	972.65
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
unit cell dimens	a = 9.9604(10) Å	a = 10.440(2) Å
	b = 15.3873(14) Å	b = 13.114(3) Å
	c = 26.682(3) Å	c = 15.172(3) Å
	α = 90°	α = 80.508(12)°
	β = 92.738(8)°	β = 80.789(14)°
	γ = 90°	γ = 75.243(14)°
volume, Z	4112.3(7) Å^3, 4	1965.9(7) Å^3, 2
density (calcd)	1.592 Mg/m^3	1.643 Mg/m^3
abs coeff	3.72 mm^{-1}	3.88 mm^{-1}
cryst habit	colorless prism	yellow tablet
cryst size	0.45 × 0.35 × 0.30 mm^3	0.25 × 0.15 × 0.06 mm^3
index ranges	$0 \le h \le 12$	$-12 \le h \le 12$
	$-18 \le k \le 4$	$-14 \le k \le 15$
	$-31 \le l \le 31$	$-17 \le l \le 18$
no. of reflns collected	9551	9128
no. of ind reflns	7225 [R(int) = 0.024]	6910 [R(int) = 0.058]
min. and max. transmn	0.71 and 0.86	0.76 and 0.92
no. of restraints/params	457/520	481/514
goodness-of-fit on F^2	0.89	0.84
wR2 (all data)	0.060	0.063
R1 [$I > 2\sigma(I)$]	0.031	0.038
largest diff peak and hole	1.13 and −0.44 e Å^{-3}	0.99 and −0.70 e Å^{-3}

Results and Discussion

Syntheses of Complexes. The aryl(ethynyl)aurate(I) complexes PPN[Au(Ar)(C≡CH)] [Ar = C_6F_5 (**1**), $C_6H_4NO_2$-2 (**2**), $C_6H_2(NO_2)_3$-2,4,6 (**3**)] were obtained by treating PPN[Au(Ar)Cl] (Ar = C_6F_5, $C_6H_4NO_2$-2, $C_6H_2(NO_2)_3$-2,4,6)[20] with Tl(acac), removing TlCl by filtration, and bubbling ethyne through the resulting solution (Scheme 1). The reactions proceeded equally well in dichloromethane or acetone, and complexes **1** and **2** were obtained in high yield (80% **1** and 88% **2**), while the yield for **3** is only moderate due to its lower stability. It is reasonable to assume that these reactions occur through the formation of the corresponding acetylacetonato complexes **A**, which would react in situ with an excess of ethyne to give complexes **1**−**3**. These are new examples of the utility of acetylacetonatogold(I) compounds in the synthesis of a wide variety of gold(I) complexes, by deprotonating organic substrates containing even weakly acidic hydrogen atoms.[21] The aryl(acetylacetonato)gold(I) intermediates seem to be stable in solution, but all attempts to isolate them led to

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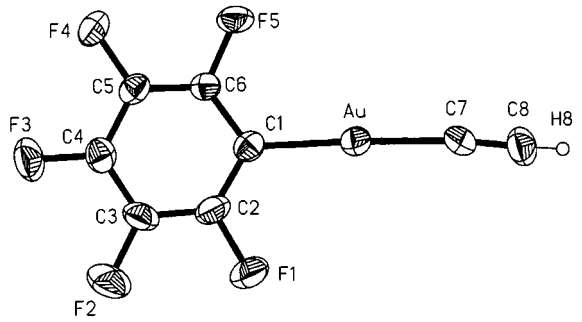


Figure 1. Thermal ellipsoid plot of the anion of **1** (50% probability levels) with the labeling scheme. Selected bond lengths (Å) and angles (deg): Au−C(7) 1.984(6), Au−C(1) 2.049(5), C(7)−C(8) 1.175(8), C(7)−Au−C(1) 176.9(2), C(8)−C(7)−Au 174.6(5).

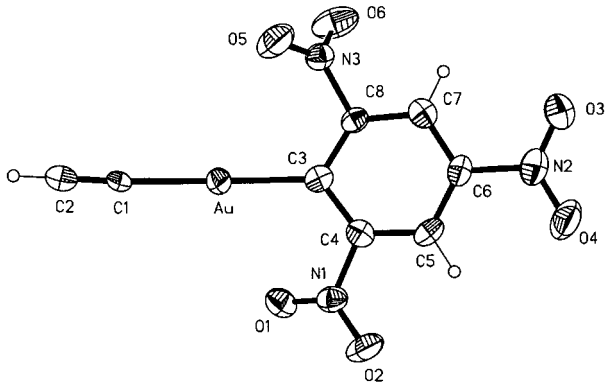
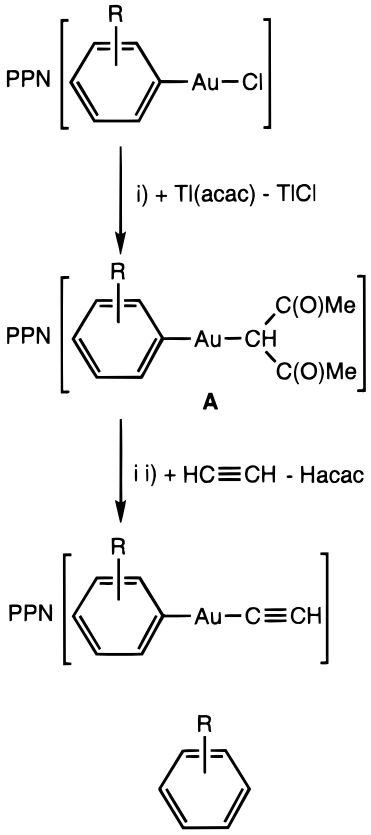


Figure 2. Thermal ellipsoid plot of the anion of **3** (50% probability levels) with the labeling scheme. Selected bond lengths (Å) and angles (deg): Au−C(1) 2.0148(56), Au−C(3) 2.0392(54), C(1)−C(2) 1.1469(73), N(1)−O(1) 1.2118-(54), N(1)−O(2) 1.2166(54), N(2)−O(4) 1.2180(59), N(2)−O(3) 1.2212(61), N(3)−O(6) 1.2123(55), N(3)−O(5) 1.2156(53), C(1)−Au−C(3) 175.5(2), C(2)−C(1)−Au 175.6(5).

extensive decomposition to give colloidal gold.

The reaction (in acetone, 48 h) between equimolar amounts of PPN[Au(C_6F_5)(C≡CH)] (**1**) and PPN[Au-(C_6F_5)Cl] and a small excess of KOH leads, after concentration to dryness, extraction with dichloromethane, filtration of the extract, concentration of the resulting solution, and addition of *n*-pentane, to a white precipitate. Its $^{13}C\{^1H\}$ NMR spectrum [δ 88.20 (s, AuC) ppm], elemental analyses [found: C, 56.60; H, 3.28; N, 1.05; calcd for $C_{86}H_{60}Au_2F_{10}N_2P_4$: C, 56.47; H, 3.31; N, 1.53], molar conductivity in acetone [Λ_M, 196 $\Omega^{-1}cm^2$ mol^{-1} (5.6×10^{-4} mol L^{-1})], and mass spectrum ((FAB, negative ion mode): *m*/*z* (% abundance) 752 (M^{2-}, 18.8), 389 ([C_6HAuF_5]$^-$ 20.9), 531 ([$C_{12}AuF_{10}$]$^-$, 100)) are in agreement with its formulation as a dinuclear complex, PPN_2[{Au(C_6F_5)}$_2$(μ-C≡C)]. Thus we assumed that the [Au(C≡C)(C_6F_5)]$^{2-}$ ligand resulting from deprotonation of the terminal alkyne complex **1** by the base KOH displaced the chloro ligand present in PPN[Au(C_6F_5)-Cl] to give the dinuclear complex with concomitant formation of insoluble KCl. However, the $^{19}F\{^1H\}$ NMR spectrum indicates the presence of two different types of C_6F_5 groups in an approximately 2:1 ratio [the more abundant one gives resonances to −113.96 (m, *o*-F), −164.20 (t, *p*-F), and −165.01(m, *m*-F) ppm and the other one at −115.37 (m, *o*-F), −163.15 (t, *p*-F), and −164.49 (m, *m*-F) ppm]. None of these resonances correspond to the starting pentafluorophenyl complexes. Recrystallization of this compound (or mixture), whereby some decomposition to give colloidal gold is observed, leads always to the same result. We also attempted the synthesis of the dinuclear complex using diethyl- or triethylamine as the base, but in both cases complex mixtures formed, which could not be separated. We have previously described[16b] the syntheses of neutral mononuclear [Au(C≡CR)(L)] (R = $SiMe_3$, Bu^t, L = PPh_3, PCy_3, $CNBu^t$) or dinuclear [$(AuL)_2$\{μ-C≡$C(CH_2)_5$C≡C\}] (L = PPh_3, $CNBu^t$) alkynyl complexes by reacting [AuCl-(L)] and the corresponding alkyne or dialkyne in the presence of a base. On that occasion we used $NHEt_2$ or NEt_3 interchangeably, except in the case of L = Bu^t-NC, for which $NHEt_2$ must be excluded to avoid formation of the carbene complex [Au(C≡CR){C(NHBu^t)-NEt_2}] by attack of the secondary amine $NHEt_2$ on the isocyanide ligand.

Scheme 1



1 C_6F_5
2 $C_6H_4NO_2$-2
3 $C_6H_2(NO_2)_3$-2,4,6

Structure of Complexes. As far as we are aware, complexes **1** and **3** are the first ethynylgold complexes characterized by X-ray diffraction methods. Both crystal structures display the dicoordinate gold atom in a quasi linear environment with C−Au−C angles of 176.9(2)° (**1**) and 175.5(2)° (**3**). The Au−C≡C bond angle [**1**, 176.9-(2)°; **3**, 175.5(2)°] is also slightly bent, as is the case in most alkynylgold(I) complexes; values as low as 172-(1)°[22] or 173.5(6)° [23] are not infrequent. The Au−$C_{ethynyl}$

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[1.984(6) (**1**), 2.015(6) (**3**) Å] and the C≡C [1.175(8) (**1**), 1.147(7) (**3**) Å] bond distances are slightly longer and shorter, respectively, with respect to the mean value found for a series of alkynylgold complexes[1d,7a,9a,e,13,15,16b,23,24] (mean $Au-C_{alkynyl}$, 1.97 Å, mean $C\equiv C_{Au}$, 1.199 Å). The lengthening of the $Au-C_{ethynyl}$ bond distance could be due to the greater trans influence of the aryl ligand than the usual ligands in other alkynylgold complexes. The strengthening of the C≡C bond in ethynyl with respect to other alkynyl ligands had been previously observed in complexes of other elements.[25]

In complex **1**, the C−C [1.350(6)−1.387(6) Å] and C−F [1.342(5)−1.372(5) Å] bond distances within the pentafluorophenyl ring are normal.[20,26] The $Au-C_{aryl}$ bond distance [2.049(5) Å] is similar to those found in other pentafluorophenylgold(I) complexes with methanide,[27] carbene,[28] or aryl[26c] ligands but longer than in complexes with sulfur[20] or nitrogen[26a] donor ligands, consistent with the stronger trans influence of carbon donor ligands. The bond angles in the pentafluorophenyl ring are in the range 112.7(5)−125.3(5)°, the smallest angle being centered at the ipso carbon. This distortion has been previously observed in other aryl complexes, including pentafluorophenylgold derivatives;[26a,27,29] its magnitude depends on the nature of the ring substituents, and it has been accounted for[19,30] in terms of Bent's isovalent hybridization concept.[31]

In complex **3**, the C−C [1.382(7)−1.403(7) Å], C−N [1.474(7)−1.492(7) Å], and N−O [1.212(6)−1.221(6) Å] bond distances within the aryl ring are in the range found in those few trinitrophenyl complexes structurally characterized.[19,30,32] The $Au-C_{aryl}$ bond distance in **3** [2.039(5) Å] is similar or slightly longer, respectively, compared to those found in $[Au(SbPh_3)_4][Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}_2]$ [2.041(13) and 2.015(12) Å] or $[Au\{C_6H_2(NO_2)_3\text{-}2,4,6\}(dmphen)]$ (dmphen = 2,9-dimethyl-1,10-phenanthroline) [2.000(3) Å]—which are the only two other trinitrophenylgold(I) complexes available for comparison[19]—as expected for carbon or nitrogen donor ligands trans to the $Au-C_{aryl}$ bond, respectively. In complex **3**, the presence of the three electron-withdrawing nitro groups causes severe distortion of the aromatic angles, mainly affecting the angle centered at the carbon atom bonded to the metal [C8−C3−C−4, 111.0(5)°]. The narrowing of the endocyclic angle at the ipso carbon [in the range 108.9(11)[19]−113.7(10)° [30a]] is a common feature for trinitrophenyl complexes and has been accounted for in the same terms as mentioned for **1**.[19,30] The rotation of the nitro groups with respect to the mean plane of the phenyl ring observed in **3** [23.9° and 54.6° for the nitro groups ortho to the gold atom and only 7.3° for that in the para position] is similar to that found in other nitro-[33] and trinitrophenyl complexes.[30,32]

NMR and IR Spectra. In complexes **1**−**3** the resonances due to the ethynyl proton [at δ 1.59 (**1**), 1.52 (**2**), and 1.57 (**3**) ppm] is in the range found for other ethynylgold complexes (δ 1.37−1.81 ppm),[16b] highfield shifted in all cases with respect to that of ethyne (δ 1.80 ppm). This suggests that the arylgold fragment attached to the −C≡CH moiety is less electronegative than the proton. The $^{13}C\{^1H\}$ NMR spectra of complexes **1**−**3** show the ethynyl carbon nuclei in the ranges δ 65.77−90.05 (≡CH) and δ 88.20−127.10 (AuC≡) ppm. Other anionic ethynylgold(I) complexes show the analogous resonances in the ranges δ 82−87 and δ 103−127 ppm.[16b]

The IR spectra of complexes **1**−**3** show one $\nu_{C\equiv C}$ stretching band [at 1970 m (**1**), 1968 w (**2**), 1962 w (**3**) cm^{-1}] slightly shifted to low energy with respect to that of ethyne [at 1974 cm^{-1} (Raman)].[34] This effect suggests that the arylgold moieties exert +I or +M effects, which would be enhanced by the anionic character of the complexes. This has been observed in other anionic ethynylgold complexes.[16b] The spectra show also the corresponding ν_{CH} stretching mode as a weak band [at 3268 (**1**), 3284 (**2**), 3259 (**3**) cm^{-1}] in the range previously reported for ethynyl complexes of gold or other elements.[16b,25] The IR spectra show also strong or medium absorptions characteristic of the pentafluorophenyl[35] (**1**: 1498, 948, 788 cm^{-1}) or nitrophenyl[18] (**2**: 1504; **3**: 1530, 1514 cm^{-1}) ligands.

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Supporting Information Available: Atomic positional parameters for the freely refined atoms, bond lengths and interbond angles, atomic displacement parameters, and hydrogen atom parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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