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Synthesis and solution behavior of the trinuclear palladium(II) unsaturated carboxylate complexes *triangle*- $Pd_3[\mu-O_2CC(R') = CHMe]_6 (R' = Me, H)$: X-ray structure of palladium(II) tiglate (R' = Me)

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Abstract

The first examples of binary palladium(II) derivatives of unsaturated carboxylic acids are reported. It was found that the interaction of Pd₃(μ -OAc)₆ with the α , β -unsaturated 1-methylcrotonic (tiglic) and crotonic acids leads to the corresponding carboxylates of composition Pd₃[μ -O₂CC(R') = CHMe]₆, where R' = Me (1) or H (2). The new compounds have been characterized by elemental analysis, solid and solution IR, ¹H and ¹³C NMR, and ESI mass spectrometry. The crystal structure of 1 has been determined. This molecule displays a central Pd₃ cyclic core with Pd–Pd distances of 3.093–3.171 Å. Each Pd–Pd bond is bridged by a pair of carboxylate ligands, one above and the other below the Pd₃ plane, providing a square planar coordination for each Pd atom in an approximate D_{3h} overall symmetry arrangement. Solution spectroscopic data show that the bridging $\eta^1:\eta^1:\mu_2$ interaction of the carboxylates of 1 and 2 is readily displaced, with a change of the ligand to the terminal (η^1) coordination mode.

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1. Introduction

Binary (or homoleptic) palladium carboxylates find a wide range of uses both in research and in practical applications [1]. These compounds, especially palladium acetate, serve as starting materials for catalyst preparation for many kinds of reactions, or as stoichiometric reagents in stereoand regioselective synthesis. However, in spite of several

* Corresponding author. *E-mail address:* campora@iiq.csic.es (T.A. Stromnova). decades of investigation (palladium acetate was first obtained in 1965) there is a paucity of compounds of this type. To date only 6 homoleptic palladium carboxylates $Pd_3(O_2CR)_6$ (R = Me, Et, ^{*t*}Bu, *rac*-EtCH(Me), CF₃, and 2,4,6-C₆H₂Me₃) have been structurally characterized [2–9]. To our knowledge, no homoleptic carboxylates of palladium displaying unsaturated R groups are known, although a few examples or complexes of composition $PdL_2(O_2CR)_2$ (R = unsaturated group) have been reported [10,11]. In principle, unsaturated carboxylates may display different coordination modes due to the presence of two potentially binding sites, the carboxylate and the olefin functionalities.

Unsaturated Pd carboxylates could display superior properties as catalyst precursors, since the ability of the unsaturated carboxylate ligand to coordinate through π interactions could facilitate reductive decomposition pathways, and contribute to stabilize the resulting Pd(0) species. In this paper we describe for the first time the synthesis and characterization of two examples of α , β -unsaturated palladium carboxylates, Pd₃(μ -O₂CC(R') = CHMe)₆, namely the tiglate (1-methylcrotonate, R' = Me, 1) and the crotonate (R' = H, 2).

2. Results and discussion

2.1. Synthesis

Among the general methods available for the synthesis of metal carboxylates, the reaction of palladium acetate with higher carboxylic acids represents a very convenient method for the preparation of a wide range of palladium derivatives. As shown in Eq. (1), this method allows the synthesis of the desired compounds 1 and 2. Thus, upon treatment of palladium acetate with a 2-3 fold excess of tiglic or crotonic acid at 60 °C during 2 h in toluene, a gradual darkening of the reddish color of the solution was observed. After workup, compounds 1 and 2 were isolated as dark red or dark yellow microcrystalline solids, respectively. Elemental analysis data for these compounds agree with the expected composition, $Pd(O_2CR)_2$. They have good solubility and stability in non-polar organic solvents (CH₂Cl₂, benzene), but are sparingly soluble in polar solvents such as ethanol, acetone or water.



2.2. Structure of the carboxylate complexes

The IR spectra of both substances display intense bands due to the asymmetric (v_{as}) and symmetric (v_{sym}) C–O stretching vibration modes of the carboxylate groups. The v_{as} appears at 1582 cm⁻¹, and v_{sym} at ca. 1410 cm⁻¹ (1408 cm⁻¹ for **1** and 1414 cm⁻¹ for **2**). The difference between the two vibration frequencies, Δv , is small, ca. 170 cm⁻¹, pointing out to a bridging coordination mode of the carboxylate groups ($syn,syn-\eta^1:\eta^1:\mu_2$) [11–13]. The relatively low value of v_{as} contrasts with the higher value characteristic of the analogous band in saturated palladium carboxylates, which is placed above 1600 cm⁻¹. Obviously, this effect can be explained by the conjugation of the carboxylato and olefin functionalities. Conversely, the C=C stretching absorption appears at 1655 cm⁻¹, very close to those corresponding to the free tiglic (1643 cm^{-1}) and crotonic (1654 cm^{-1}) acids. This observation suggests the absence of Pd–olefin π interactions.

Attempts to record the ESI-MS spectra of the two carboxvlates have been carried out using different solvents, but best results were obtained in CH₂Cl₂. The spectra did not show peak clusters assignable to the molecular ions, however several signals were detected in both cases. These signals show the characteristic isotopic peak pattern expected for monocationic species containing the Pd₃ unit, indicating that both compounds exist as trimers in solution. Simulations of the isotopic peak distributions of the resulting Pd_3L_n positive ions show an excellent agreement with the experimental data. The spectrum corresponding to compound 1 is shown in Fig. 1. Two main peak clusters are observed at m/z 880 (I = 98%) and 854 (I = 100%), and a less intense one at m/z 814 (I = 19%). Whilst the latter can be attributed to the ion $[Pd_3(O_2CR')_5]^+$, resulting from the loss of one carboxylate group, the assignation of the two more intense peaks is more difficult. However, we tentatively propose that both the m/z 880 and 854 ions could arise from complexation of the carboxylate molecule with a Na⁺ cation (present in the solvent in trace amounts), followed by loss of the neutral fragments R'H and OCC-MeCMe, respectively.

Compound 2 behaves similarly to 1 under electrospray ionization conditions, and its mass spectrum consists of three partially overlapping clusters at m/z 812 (I = 93 %), 796 (I = 100%) and 784 (I = 98 %); the first and the latter can also be explained as the result of analogous processes. i.e., Na⁺ complexation and loss of R'H and OCCHCMe, respectively.

The analytical, solid state IR and ESI-MS spectroscopy data strongly suggest that both palladium tiglate and crotonate display a trimeric structure with bridging palladium acetate groups, analogous to those displayed by other palladium carboxylates. This has been confirmed by the crystal structure of compound 1, shown in Fig. 2. The molecule exhibits a cyclic Pd₃ core with Pd-Pd distances within the range 3.0930-3.1707 Å (Table 1). Each Pd-Pd bond is bridged by a pair of carboxylate ligands, one above and the other below the Pd₃ plane, providing a slightly distorted square planar coordination for each Pd atom in an approximate D_{3h} overall symmetry arrangement. Each Pd atom is shifted from the O_4 plane by 0.21–0.22 Å (Pd1: 0.212 Å; Pd2: 0.211 Å; Pd3, 0.219 Å) towards the centre of the Pd₃ triangle. The lengths of the uncoordinated C=C bonds are somewhat variable and are between 1.303(6) Å (C27–C28) and 1.346(7) Å (C7–C8). However, the average C=C length, 1.31(2) Å, is indistinguishable of that of tiglic acid (1.315 Å) [14]. This is in contrast with the slight elongation of the double bond observed in some unsaturated metal carboxylates [15].

The three Pd–Pd bonds in 1 are fairly similar, although the Pd(1)–Pd(2) (3.1707(4) Å) is slightly longer than the other two (3.1112(4), 3.0930(4)). In general, the reported structures of trimeric palladium carboxylates show some



Fig. 1. (a) ESI-MS spectrum of a CH₂Cl₂ solution of 1, displaying tentative peak assignations ($R' = C_4H_7$). (b) Expansion of the m/z 854 peak, showing the characteristic Pd₃ isotopic pattern. (c) Simulation of the latter peak for a composition $C_{25}H_{36}NaO_{11}Pd_3$.

differences in the Pd–Pd bonds, causing the Pd_3 core to vary from an equilateral to isosceles triangular arrangement. The source of this variability probably stems from the fact that these compounds crystallize in widely different space groups, some of which impose crystallographic symmetry on the molecule.



Fig. 2. Crystal structure of palladium tiglate (1).

2.3. Solution behavior of the carboxylate complexes

The ¹H and ¹³C{¹H} of compounds 1 and 2 in dry C_6D_6 display essentially one set of signals in each case, corresponding to the tiglate and crotonate organic fragment. The resonances corresponding to the olefin functionality are found in positions that do not differ substantially of those of the free acids. For example, the sp^2 -C signals of 1 and 2 appear 1–4 ppm upfield of those of free tiglic and crotonic acids in their ${}^{13}C{}^{1}H$ spectra. This observation suggests the absence of any significant Pd–olefin π interactions, which would be expected to cause larger upfield coordination shifts. Together with the main set of signals, low intensity sets of bands (ca. 5% of the main signals) can be observed. These signals increase their intensity in the ¹H NMR spectra recorded in CD₂Cl₂ to ca. 20% of those main species. The shape and coupling constants of the main set of signals is reproduced in the secondary ones, indicating that the new species contain unaltered carboxylato groups (Fig. 3).

The IR spectra of **1** and **2** in C_6D_6 display the same bands observed in the solid state, such as the characteristic v_{as} , v_{sym} and $v_{C=C}$ absorptions, at nearly unchanged frequencies, indicating that the trinuclear structure with bridging carboxylate ligands is conserved in solution. However, a few new weak bands are also observed, whose relative intensity increases in CD₂Cl₂. Among these, new bands at 1535 cm⁻¹ and two at 1287, 1262 cm⁻¹ are observed for **1** and at close-by positions for **2**. Assuming that these bands can be assigned to PdOCO absorptions in the secondary species, the large value of the associated Δv parameters (ca. 250 cm⁻¹) suggests that some of the bridging

Table 1 Selected bond lengths and angles for compound 1

Bond lengths (Å)			Bond angles (°)				
Pd(1)–Pd(3)	3.1112(4)	C(7)–C(8)	1.346(7)	Pd(3)–Pd(1)–Pd(2)	58.983(8)	O(6)–Pd(3)–O(10)	84.40(11)
Pd(1) - Pd(2)	3.1707(4)	C(12) - C(13)	1.313(6)	Pd(3)-Pd(2)-Pd(1)	59.550(8)	O(12)-Pd(3)-O(8)	85.74(11)
Pd(2) - Pd(3)	3.0930(4)	C(17) - C(18)	1.332(6)	Pd(2)-Pd(3)-Pd(1)	61.467(8)	O(6) - Pd(3) - O(8)	93.76(11)
Pd(1)–O(7)	1.992(2)	C(22) - C(23)	1.323(6)	O(7) - Pd(1) - O(3)	170.17(11)	O(10)-Pd(3)-O(8)	163.31(10)
Pd(1)–O(3)	1.998(3)	C(27)-C(28)	1.303(6)	O(7)-Pd(1)-O(5)	90.66(10)	O(1)-C(1)-O(2)	126.4(3)
Pd(1)–O(5)	2.012(2)	O(1)–C(1)	1.261(4)	O(3)-Pd(1)-O(5)	85.60(11)	O(3)-C(6)-O(4)	126.3(3)
Pd(1) - O(1)	2.021(2)	O(2) - C(1)	1.266(4)	O(7) - Pd(1) - O(1)	87.67(10)	O(5)-C(11)-O(6)	125.6(3)
Pd(2) - O(2)	1.976(2)	O(3)–C(6)	1.262(5)	O(3) - Pd(1) - O(1)	93.63(11)	O(8)-C(16)-O(7)	126.3(3)
Pd(2)–O(9)	1.983(3)	O(4)–C(6)	1.265(5)	O(5) - Pd(1) - O(1)	165.19(10)	O(9)-C(21)-O(10)	125.7(3)
Pd(2) - O(4)	2.013(3)	O(5)–C(11)	1.264(4)	O(2) - Pd(2) - O(9)	171.17(10)	O(11)-C(26)-O(12)	125.7(3)
Pd(2)–O(11)	2.019(3)	O(6)–C(11)	1.271(4)	O(2)-Pd(2)-O(4)	93.05(10)	C(3) - C(2) - C(5)	124.4(3)
Pd(3)–O(12)	1.984(3)	O(7)–C(16)	1.268(4)	O(9) - Pd(2) - O(4)	85.13(10)	C(8)-C(7)-C(10)	125.1(4)
Pd(3)–O(6)	1.991(3)	O(8)–C(16)	1.261(4)	O(2)-Pd(2)-O(11)	85.60(10)	C(13)-C(12)-C(15)	124.4(3)
Pd(3)–O(10)	2.003(2)	O(9)–C(21)	1.261(4)	O(9) - Pd(2) - O(11)	93.86(10)	C(18)-C(17)-C(20)	125.5(4)
Pd(3)–O(8)	2.006(3)	O(10) - C(21)	1.268(4)	O(4) - Pd(2) - O(11)	164.62(10)	C(23)-C(22)-C(25)	126.5(4)
C(2) - C(3)	1.311(5)	O(11)–C(26)	1.264(4)	O(12)-Pd(3)-O(6)	171.48(10)	C(28)-C(27)-C(30)	125.7(4)
		O(12)–C(26)	1.268(4)	O(12)–Pd(3)–O(10)	93.64(11)	O(12)–Pd(3)–O(10)	93.64(11)



Fig. 3. ¹H NMR spectrum of compound 2 in C_6D_6 (a) and CD_2Cl_2 (b).

carboxylate ligands rearrange from bridging to terminal coordination. As shown in Fig. 4, such a rearrangement requires an additional ligand to compensate for the reduced electron donor capability of the carboxylate



Fig. 4. Different coordination modes of the carboxylate ligand in solution.

group. Again, palladium-olefin π interactions are unlikely to be involved, as the secondary olefin proton resonances are shifted by less than 0.5 ppm from their parent signals. A similar behavior has been detected for other carboxylate derivatives, particularly for palladium acetate where it has been explained as a result of the partial displacement of the bridging acetate by traces of water present in the solvent (L = H₂O, in Fig. 4) [8]. This is likely to be also the case for **1** and **2** in CD₂Cl₂ as well, since this solvent was not rigorously dried for this work. In fact, v_{OH} bands are clearly observed at 3689 and 3520 cm⁻¹ in the IR spectrum of **1** in CD₂Cl₂, although other characteristic bands of the aquo ligand (~ 1630 , $\sim 600 \text{ cm}^{-1}$) [16] are more difficult to observe or assign due to their proximity to other intense absorptions.

3. Conclusions

The interaction of $Pd_3(\mu$ -OAc)₆ with unsaturated 1-methylcrotonic (tiglic) and crotonic acids has been studied. This reaction leads to the complexes $Pd_3[\mu-O_2C(Me)C =$ CHMe]₆ and Pd₃[μ -OCOCH = CHMe]₆, the first homoleptic palladium derivatives containing unsaturated carboxylate groups. This study showed that among two possible interaction modes of unsaturated carboxylates, i.e., classic μ -carboxylate bridging or Pd–olefin π bonding, only the former occurs. However, π -interactions could be important for the reactivity of such carboxylate complexes, facilitating reductive processes leading to more stable Pd(0) species. In addition, 1 and 2 display prochiral centers in the α - and β-position of the unsaturated carboxylate groups. Therefore, the availability of these compounds opens interesting perspectives for new applications of Pd carboxylates either as stoichiometric reagent or catalytic precursors for the synthesis of new organometallic and organic compounds.

4. Experimental

4.1. Reagents and physical measurements

Palladium(II) acetate was prepared by the oxidation of palladium black with concentrated HNO₃ in glacial acetic acid according to a known procedure [2] and unsaturated acids were purchased from Acros Organics, Belgium, and used without further purification. All organic solvents were purified and dried according to standard procedures. C_6D_6 was refluxed over sodium benzophenone ketyl, transferred to a glass ampoule under vacuum at room temperature and kept under nitrogen atmosphere. Similarly, CD₂Cl₂ was degassed, transferred in vacuo and stored under nitrogen. Microanalyses were conducted on a Carlo Erba Analyser CHND-OEA 1108. The spectroscopic instruments used were a Carl Zeiss SPECORD-M82 (KBr pellets) and Bruker Model Vector 22 for IR spectra, and Bruker DPX-300, DRX-400 NMR spectroscopy. ¹³C{¹H} NMR assignments were helped in most cases with the use of gated-decoupling techniques. The ESI-MS were recorded on a Finnigan MAT LCQ Deca operating in the positive ion mode with full scanning in the range [150.00-2000.00].

4.2. Preparation of $Pd_3[\mu - OCO(Me)C = CHMe]_6(1)$

An excess of tiglic acid (690 mg, 6.9 mmol) was added to a solution of $Pd_3(\mu$ -OCOMe)₆ (672 mg, 3 mmol based on $Pd(OCOMe)_2$ unit) in toluene (50 ml). The resulting suspension dissolved rapidly (within ca. 3 min) to give a bright orange-red solution. The solution was stirred at 60 °C for 2 h, during which time its color is changed on dark-red. The reaction mixture was filtered to remove a small amount of black solid, the solution was concentrated on a rotary evaporator to $\sim 1/3$ volume and stored at -18° . Large dark-red crystals were formed after 1-2 weeks at this temperature. The crystals were removed and the solution was slightly concentrated and cooled at -18 °C, to yield a second crop of crystals. The operation was repeated 3-4 times and dark-red powdery crops were obtained. The elemental analyses and IR spectra of the crystalline and powder samples were indistinguishable. The product is soluble in most organic solvents. The combined yield of $Pd_3[\mu-OCO(Me)C = CHMe]_6$ was 94 mg (10% on Pd). ¹H NMR (C₆D₆, 20 °C, 300 MHz): δ 1.15 (d, 3H, ${}^{3}J_{\rm HH} = 7.1$ Hz, Me); 1.61 (s, 3H, Me); 6.77 (q, 1H, C=CH). ${}^{13}C{}^{1}H{}$ (C₆D₆, 75 MHz, 20 °C): 12.5 (Me); 13.4 (Me); 129.9 (= $C(Me)CO_2$); 137 (=C(H)Me), 184.1 (CO₂). Anal. Calc. for C₃₀H₄₂O₁₂Pd₃: C, 39.42; H, 4.60. Found: C, 39.53; H, 4.39%. IR (KBr, cm⁻¹): 1655s $(v_{(C=C)})$, 1582vs $(v_{as(CO)})$, 1408vs $(v_{s(CO)})$. IR (CD_2Cl_2) , cm⁻¹): 3687m, 3521m (v_{O-H}, second. species), 1721m, 1688m (second. species); 1652s ($v_{(C=C)}$, prim. species); 1583vs ($v_{as(CO)}$, prim. species), 1535m ($v_{C=O}$, second. species); 1410vs (v_{sym(CO)}, prim. species), 1290m, 1267m (v_{C-O}, second. species).

4.3. Preparation of $Pd_3[\mu - OCOCH = CHMe]_6(2)$

This compound was prepared analogously to 1 (2 mmol scale based on Pd(OCOMe)₂), but a slightly different procedure was followed for product separation. The reaction mixture was evaporated to dryness. The oily residue was solidified by stirring with hexane (1:3 on volume) for 1 hour followed by evaporation under reduced pressure. This operation was repeated 3-4 times. During these operations the oil was gradually transformed into an off-yellow powder which was dried under vacuum for 2-3 h. The solid was washed with pentane, filtered off and the solid dried under vacuum to produce dark-yellow powder. The compound is soluble in most organic solvents. The yield of $Pd_3[\mu$ -OCOCH = CHMe]₆ was 220 mg (40% on Pd). ¹H NMR (C₆D₆, 20 °C, 300 MHz): δ 1.10 (d, 3H, ${}^{3}J_{HH} = 6.8$ Hz, Me); 5.60 (d, 1H, ${}^{3}J_{\text{HH}} = 15.4 \text{ Hz}, \text{CH}=\text{CHMe}); 6.64 (dq, 1H, \text{CH}=\text{CHMe}).$ ¹³C{¹H} (C₆D₆, 75 MHz, 20 °C):16.7 (Me); 123.5 (=CHMe); 143.6 (=CHCO₂); 182.7 (CO₂). Anal. Calc. for C₂₄H₃₀O₁₂Pd₃: C, 34.73; H, 3.62. Found: C, 34.60; H, 3.44%. IR spectrum (KBr, cm⁻¹): 1656m ($v_{(C=C)}$), 1582vs $(v_{as(COO)})$, 1414vs $(v_{s(COO)})$. IR $(CD_2Cl_2, \text{ cm}^{-1})$: 3690m, 3518m (v_{O-H}, second. species), 1727m, 1701m (second. species); 1657s ($v_{(C=C)}$, prim. species); 1588vs ($v_{as(CO)}$, prim. species), 1549m ($v_{C=O}$, second. species); 1415vs ($v_{svm(CO)}$, prim. species), 1300m, 1264m (v_{C-O} , second. species).

4.4. X-ray diffraction study of 1

X-ray data for a red single-crystal of 1 with dimensions $0.46 \times 0.42 \times 0.27$ mm were collected on an Bruker-Nonius X8Kappa diffractometer equipped with an Apex-II CCD

Table 2

Crystal data and structure refinement for complex ${\bf 1}$

Empirical formula	C ₃₀ H ₄₂ O ₁₂ Pd ₃
Formula weight	913.84
Temperature (K)	273(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	10.2482(7)
b (Å)	19.6502(13)
<i>c</i> (Å)	17.5670(11)
β (°)	93.480(2)
$V(\text{\AA}^3)$	3531.1(4)
Ζ	4
D_{calc} (Mg/m ³)	1.719
μ (Mo K α) (mm ⁻¹)	1.568
<i>F</i> (000)	1824
Crystal size (mm)	$0.46 \times 0.42 \times 0$.27
θ Range for data collection (°)	3.06-30.26
Index ranges	$-14 \leq h \leq 14$,
	$-27 \leqslant k \leqslant 27,$
	$-24 \leqslant l \leqslant 24$
Reflections collected	67819
Independent reflections $[R_{int}]$	10404 [0.0361]
Completeness to $\theta = 30.26^{\circ}$, %	98.6
Maximum and minimum transmission	0.6769 and 0.5324
Data/restraints/parameters	10404/0/406
Goodness-of-fit (S) ^a on F^2	1.026
Final <i>R</i> indices $[I > 2\sigma(I)]^{b,c}$	$R_1 = 0.0398; wR_2 = 0.0962$
$R^{b,c}$ indices (all data)	$R_1 = 0.0492; wR_2 = 0.1007$
Largest difference in peak and hole ($e \text{ Å}^{-3}$)	2.555 and -1.131

^a $S = \left\{ \sum [w(F_o^2 - F_c^2)^2]/(n-p) \right\}^{1/2}$; (*n* = number of reflections, *p* = number of parameters).

^b $R_1(F) = \sum (|F_o| - |F_c|) / \sum |F_o|$ for the observed reflections $[F^2 > 2\sigma(F^2)]$. ^c $wR_2(F^2) = \left\{ \sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2 \right\}^{1/2}$.

area detector, using a graphite monochromator Mo K α l ($\lambda = 0.71073$ Å) and a Bruker Cryo-Flex low-temperature device. The data were collected in the range $6.12 < 2\theta < 60.52$ ($-14 \le h \le 14$, $-27 \le k \le 27$, $-24 \le l \le 24$) using ω and ϕ scan mode. The data were reduced (SAINT) and corrected for Lorentz polarisation effects and absorption by multiscan method applied by SADABS [17,18]. The structure was solved by direct methods (SIR-2002) [19] and refined against all F² data by full-matrix least-squares techniques (SHELXL97) [20]. All non-hydrogen atoms were refined with anisotropic thermal parameters. All H atoms were placed in calculated positions and refined using a riding model. Details of X-ray structural investigations are listed in Table 2.

5. Supplementary material

CCDC 647411 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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