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Oxidative Addition of B–Br Bonds to Pd^0: Synthesis and Structure of *trans*-Bromo(boryl)palladium Complexes

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The oxidative addition of several bromoboranes to the Pd^0 species $[Pd(PCy_3)_2]$ yielded the novel palladium boryl complexes *trans*-$[(Cy_3P)_2Pd(Br)(BCat)]$ (**1**) (Cat = 1,2-dioxophenylene), *trans*-$[(Cy_3P)_2Pd(Br)(BCat')]$ (**2**) (Cat′ = Cat-4-*t*Bu) and *trans*-$[(Cy_3P)_2Pd(Br)\{B(X)X'\}]$ {X = Br, X′ = NMe_2 (**3**), Pip (**4**) (Pip = NC_5H_{10}), Mes (**5**) [Mes = 2,4,6-$(CH_3)_3C_6H_2$]}. Compounds **1**–**5** were characterized by multinuclear NMR spectroscopy in solution; single crystals for X-ray analyses were acquired from **2** and **3**, which thus allowed comparison of the structural data. The few palladium boryl complexes published so far were obtained by σ-bond metathesis; the oxidative addition of the corresponding bromoboranes to Pd^0 has not yet been reported.

Introduction

Transition-metal boryl complexes have been the subject of extensive studies due to their key role in catalytic processes including metal-catalyzed hydroboration and diboration[1] as well as selective functionalization of C–H-bonds.[2] Appropriate synthetic routes to transition-metal boryl complexes are salt elimination reactions[3] and the oxidative addition of B–H, B–B and B–E bonds (E = main-group element) to low-valent transition-metal complexes.[4] On the basis of platinum(0) precursors, a number of corresponding transition-metal boryl complexes have recently been synthesized by oxidative addition of chloro-,[5] bromo-[6] or iodoboranes.[7] The stability of these complexes of the type *trans*-$[(R_3P)_2Pt(Hal)(BX_2)]$ decisively depends on the electronic influence of the boron-bound substituents X, that is, the π-donating groups; in particular, O- and N-based moieties result in a significantly enhanced stability towards air and water with respect to alkyl and aryl substituents.[6a] In addition, a variety of these complexes presented pathways to new and unusual coordination modes for boron centred ligands. For example, the reaction of *trans*-$[(Cy_3P)_2Pt(Br)\{B(Fc)Br\}]$ (Fc = ferrocenyl) with $Na[BAr^f_4]$ [Ar^f = 3,5-$C_6H_3(CF_3)_2$] led to a T-shaped, three-coordinate platinum complex that acted as a precursor for a base-stabilized borylene complex of platinum.[8] Surprisingly, similar treatment of *trans*-$[(Cy_3P)_2Pt(Br)\{B(Mes)Br\}]$ {Mes = 2,4,6-$(CH_3)_3C_6H_2$} with $K[B(C_6F_5)_4]$ resulted in the first terminal platinum borylene complex.[9] Whereas platinum boryl complexes are numerous and well investigated, only relatively few palladium boryl complexes are known. Since the first complex of that type, [{(MeN(C_2H_4)MeN)B}(Me_3Sn)-Pd(dmpe)] {dmpe = 1,2-bis(dimethylphosphanyl)ethane}, was synthesized and structurally characterized in 1996 by the group of Tanaka,[10] the role of such species in homogeneous catalysis has been the focus of intense research.[1c] Experimental and computational studies provided evidence that the oxidative addition of B–B bonds to Pd centres is thermodynamically disfavoured; hence, the Pd-mediated borylation of organic substrates must be based on a different mechanism, as in the case of corresponding Pt catalysts.[11] Despite the interest in palladium boryls for catalysis, only little progress has been made towards the synthesis of such species.[12] The oxidative addition of boron–element bonds in particular has only been scarcely studied, and it was only successfully employed in the case of heterodinuclear borylene, transition-metal base-stabilized metalloborylene and iminoboryl complexes.[13] In this paper we report on a series of palladium boryl complexes obtained by the oxidative addition of bromoboranes to a zero-valent palladium precursor.

Results and Discussion

The compounds *trans*-$[(Cy_3P)_2Pd(Br)(BCat)]$ (**1**) (Cat = 1,2-dioxophenylene), *trans*-$[(Cy_3P)_2Pd(Br)(BCat')]$ (**2**) (Cat′ = Cat-4-*t*Bu) and *trans*-$[(Cy_3P)_2Pd(Br)\{B(X)X'\}]$ {X = Br, X′ = NMe_2 (**3**), Pip (**4**) [Pip = $N(C_5H_{10})$], Mes (**5**)} were synthesized by oxidative addition of the corresponding bromoboranes to $[Pd(PCy_3)_2]$ in either toluene or benzene solutions (Figure 1).

All compounds were characterized in solution by multinuclear NMR spectroscopy, and all display a characteristic high-field shift in the ^{31}P NMR spectrum and a slightly

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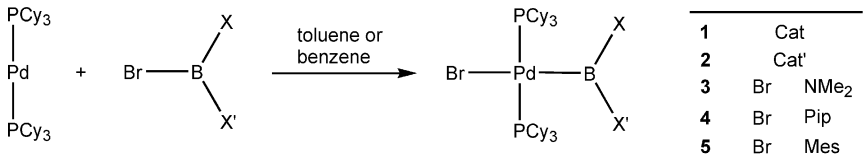

	X	X'
1	Cat	
2	Cat'	
3	Br	NMe_2
4	Br	Pip
5	Br	Mes

Figure 1. Synthesis of bromo(boryl)palladium complexes.

deshielded ^{11}B NMR resonance with respect to the palladium and borane precursors, respectively. Presumably due to unresolved coupling with the two adjacent ^{31}P nuclei in the *cis* position, the ^{11}B NMR signals of **1**–**5** are significantly broadened.[12] The compounds were isolated as air- and moisture-sensitive colourless (**1**–**3**), bright yellow (**4**) or orange (**5**) solids in yields between 73 and 82% (**1**, **3**–**5**) or 41% (**2**). As observed before,[14] bromo(boryl)palladium complexes show a significantly decreased stability with respect to their Pt congeners,[6a] and hence, complexes **1**–**4** slowly decompose in solution within 1–5 d at ambient temperature with formation of *trans*-[$(Cy_3P)_2Pd(Br)(H)$] and *trans*-[$(Cy_3P)_2PdBr_2$] as judged by the corresponding signals in the ^{31}P NMR spectra at δ = 43.6 and 26.2 ppm, respectively (Table 1).[15] In the case of mesitylboryl complex **5**, which lacks sufficient π stabilization by the boron-bound substituents, this trend becomes even more apparent; thus, **5** undergoes complete degradation within 12 h in solution.

Table 1. ^{31}P and ^{11}B NMR chemical shifts [ppm] of **1**–**5**.

Complex	δ ^{31}P	δ ^{11}B
trans-[$(Cy_3P)_2Pd(Br)(BCat)$] (**1**)	29.3	39
trans-[$(Cy_3P)_2Pd(Br)(BCat')$] (**2**)	30.6	38
trans-[$(Cy_3P)_2Pd(Br)\{B(Br)NMe_2\}$] (**3**)	24.7	42
trans-[$(Cy_3P)_2Pd(Br)\{B(Br)Pip\}$] (**4**)	26.9	40
trans-[$(Cy_3P)_2Pd(Br)\{B(Br)Mes\}$] (**5**)	19.7	89

Single crystals were obtained from a concentrated diethyl ether solution of complex **2** at –30 °C and by slow evaporation of benzene from a solution of **3** at room temperature. The structures deduced from multinuclear NMR spectroscopic data in solution were confirmed by X-ray diffraction and are presented in Figures 2 and 3. The two palladium boryl complexes crystallize in orthorhombic space groups $P2_12_12_1$ (**2**) and monoclinic $P2_1/n$ (**3**), respectively.

In both molecules, the Pd centre adopts a slightly distorted square-planar geometry and the phosphane ligands are disposed *trans* to each other. The boryl moieties as defined by the O–B–O (**2**) and N–B–Br (**3**) planes are oriented almost perpendicular to the P1–Pd1–P2-fragment [83.77° (**2**) and 71.23° (**3**)], which thus allows maximal Pd–B π-backbonding interaction. Boryl ligands exhibit a strong *trans* influence due to their σ-bonding abilities. The general trend known for platinum boryl complexes that a shorter M–B bond correlates with a shorter *trans* M–X (X = Cl, Br) bond, and hence, also with a weaker *trans* influence was observed here as well.[16] This counterintuitive finding can be explained by the fact that electronegative groups at the boryl ligand increase the s character of the Pt–B bond,

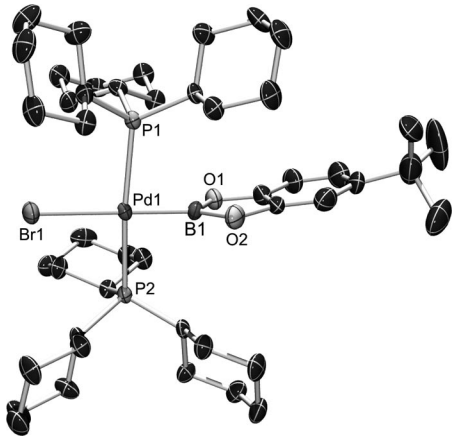

Figure 2. Molecular structure of *trans*-[$(Cy_3P)_2Pd(Br)(BCat')$] (**2**) (thermal ellipsoids at 50% probability level). Hydrogen atoms and the disorder of the Cat′ group are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–Br1 2.5729(5), Pd1–B1 1.9701(45), B1–O1 1.4061(57), B1–O2 1.4004(51), P1–Pd1–B1 86.46(15); P2–Pd1–B1 86.13(15).

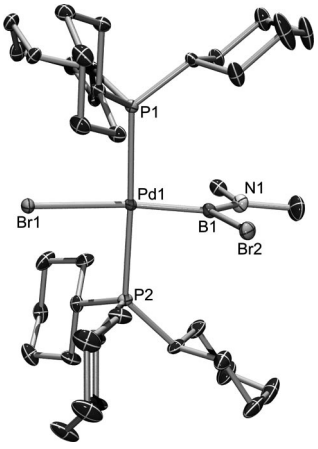

Figure 3. Molecular structure of *trans*-[$(Cy_3P)_2Pd(Br)\{B(Br)NMe_2\}$] (**3**) (thermal ellipsoids at 50% probability level). Hydrogen atoms and the disorder of the $BBrNMe_2$ group (mirrored by the PdP_2B plane) are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–Br1 2.6162(8), Pd1–B1 2.0118(71), B1–N1 1.3970(80); P1–Pd1–B1 93.79(24), P2–Pd1–B1 88.88(24).

which thus imposes a shorter metal–boron bond. Both Pd–B-separations, 1.9701(45) and 2.0118(71) Å, are in the expected range for palladium boryl complexes.[10,12] Comparison of the Pd–Br bond lengths of the two structurally characterized complexes [2.5729(5) Å for **2** and 2.6162(8) Å for **3**] show values similar to those observed for the correspond-

ing platinum boryl complexes [2.5617(10) and 2.6087(3) Å, respectively], which thus reflects the higher *trans* influence of the $B(Br)NMe_2$ ligand in comparison to that of the BCat′ moiety.[6a]

Conclusions

We synthesized and characterized palladium boryl complexes **1**–**5**, of which *trans*-[$(Cy_3P)_2Pd(Br)(BCat')$] (**2**) and *trans*-[$(Cy_3P)_2Pd(Br)\{B(Br)NMe_2\}$] (**3**) yielded suitable crystals for X-ray analysis. Investigations on the structural data revealed a higher *trans* influence of the $B(Br)NMe_2$ ligand than that of the BCat′ ligand. The compounds were synthesized by oxidative addition of bromoboranes to a Pd^0 precursor and therefore present the first palladium boryl complexes obtained by this method. In comparison to their platinum congeners, the title compounds are characterized by a significantly enhanced tendency to undergo decomposition involving cleavage of the metal–boron bond.

Experimental Section

General: All manipulations were performed under an atmosphere of dry argon or in vacuo by using standard Schlenk-line and glovebox techniques. Benzene and diethyl ether were purified by appropriate drying agents (sodium and sodium/potassium) under an atmosphere of dry argon. C_6D_6 was degassed by three freeze–pump–thaw cycles and stored over molecular sieves. NMR spectroscopic data were acquired with a Bruker Avance 500, a Bruker AMX 400 or a Bruker DRX 300 NMR spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to external TMS by the residual protiosolvent (^1H) or the solvent itself (^{13}C). $^{11}B\{^1H\}$ NMR spectra were referenced to external $BF_3{\cdot}OEt_2$ and $^{31}P\{^1H\}$ NMR spectra to 85% H_3PO_4. Microanalysis for C, H and N were performed with a Leco CHNS-932 or a vario MICRO cube Elemental Analyzer.

***trans*-[$(Cy_3P)_2Pd(Br)(BCat)$] (1):** Solid BrBCat (0.015 g, 0.075 mmol) and solid [$Pd(PCy_3)_2$] (0.050 g, 0.075 mmol) were dissolved in toluene (0.5 mL). Immediately, a fine white precipitate occurred. The slightly yellow mixture was layered with hexane (2 mL) and left in the glove box to let the solid settle down. The next day the supernatant solution was taken away, and the solid was washed with hexane (3 × 2 mL). The residual solvent was allowed to evaporate in the glove box. Compound **1** was isolated as a white solid (0.046 g, 78%).^1H NMR (500.1 MHz, CD_2Cl_2): δ = 7.14 (m, 2 H, Cat), 6.98 (m, 2 H, Cat), 2.14 (m, 6 H, Cy), 1.99–1.01 (m, 60 H, Cy) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2): δ = 149.4 (s, O_2-1,2-C_6H_4), 121.8 (s, O_2-4,5-C_6H_4), 111.7 (s, O_2-3,6-C_6H_4), 36.0 (vt, C^1, Cy), 30.4 (s, C^3, C^5, Cy), 27.9 (vt, C^2, C^6, Cy), 26.7 (s, C^4, Cy) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2): δ = 29.3 (s) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, CD_2Cl_2): δ = 39 (br. s) ppm. $C_{36}H_{66}BBrO_2P_2Pd$ (866.09): calcd. C 58.24, H 8.15; found C 57.68, H 8.37.

***trans*-[$(Cy_3P)_2Pd(Br)(BCat')$] (2):** Solid BrBCat′ (0.008 g, 0.030 mmol) was added to a pale-yellow solution of [$Pd(PCy_3)_2$] (0.020 g, 0.030 mmol) in benzene (0.5 mL). The solvent was removed in vacuo, and the yellow solid was dissolved in diethyl ether. The solvent was allowed to evaporate slowly at –30 °C in the glove box to yield **2** as colourless crystals (0.011 g, 41%). ^1H NMR (500.1 MHz, C_6D_6): δ = 7.37 (d, 1 H, Cat), 7.14 (d, 1 H, Cat), 6.92 (dd, 1 H, Cat), 2.46 (m, 6 H, Cy), 2.25–2.22 (m, 12 H, Cy), 1.80–1.44 (m, 30 H, Cy), 1.42–1.14 (m, 18 H, Cy), 1.20 [s, 9 H, C-(CH_3)$_3$] ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): δ = 150.0 (s), 147.8 (s), 145.5 (s), 118.6 (s), 110.7 (s), 109.4 (s, all C_{arom}), 36.4 (vt, C^1, Cy), 34.8 [s, $C(CH_3)_3$], 31.8 (s, CH_3), 30.8 (s, C^3, C^5, Cy), 28.0 (vt, C^2, C^6, Cy), 26.9 (s, C^4, Cy) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, C_6D_6): δ = 30.6 (s) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, C_6D_6): δ = 38 (br. s) ppm. $C_{45}H_{84}BBrO_2P_2Pd$ (922.20): calcd. C 58.61, H 9.18; found C 60.16, H 8.43.

***trans*-[$(Cy_3P)_2Pd(Br)\{B(Br)NMe_2\}$] (3):** Br_2BNMe_2 (0.020 g, 0.093 mmol) was dissolved in C_6D_6 (0.5 mL) and added to solid [$Pd(PCy_3)_2$] (0.062 g, 0.093 mmol). The light-yellow solution was layered with hexane. The solvent was allowed to evaporate slowly in the glove box. After 2 d, colourless crystals of **3** formed at room temperature (0.060 g, 73%). ^1H NMR (500.1 MHz, C_6D_6): δ = 3.24 (s, 3 H, CH_3), 2.90 (s, 3 H, CH_3), 2.78 (m, 6 H, Cy), 2.32 (m, 6 H, Cy), 2.13 (m, 6 H, Cy), 1.90–1.60 (m, 30 H, Cy), 1.45–1.20 (m, 18 H, Cy) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): δ = 46.8 (s, CH_3), 41.0 (s, CH_3), 35.7 (vt, C^1, Cy), 31.4 (br. s, C^3, C^5, Cy), 30.6 (s, C^3, C^5, Cy), 28.3 (vt, C^2, C^6, Cy), 28.2 (vt, C^2, C^6, Cy), 27.1 (s, C^4, Cy) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, C_6D_6): δ = 24.7 (s) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, C_6D_6): δ = 42 (br. s) ppm. $C_{38}H_{72}NBBr_2P_2Pd$ (881.98): calcd. C 51.74, H 8.23, N 1.58; found C 51.79, H 8.01, N 1.58.

***trans*-[$(Cy_3P)_2Pd(Br)\{B(Br)Pip\}$] (4):** Br_2BPip (0.019 g, 0.075 mmol) was dissolved into a pale-yellow solution of [$Pd(PCy_3)_2$] (0.050 g, 0.075 mmol) in benzene (2 mL) to give a yellow solution. The solvent was removed immediately in vacuo to yield **4** (0.057 g, 82%) as a bright yellow solid. ^1H NMR (300.1 MHz, C_6D_6): δ = 4.02 (m, 2 H, NC_5H_{10}), 3.60 (m, 2 H, NC_5H_{10}), 2.84 (m, 6 H, Cy), 2.09–1.62 (m, 62 H, Cy, NC_5H_{10}), 1.36–1.02 (m, 4 H, NC_5H_{10}) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ = 55.9 (s, C^2, NC_5H_{10}), 50.8 (s, C^6, NC_5H_{10}), 36.1 (vt, C^1, Cy), 31.7 (s, C^3, C^5, Cy), 31.1 (s, C^3, C^5, Cy), 28.8–28.4 (m, C^2, C^6, Cy), 27.5 (s, C^4, Cy), 26.6 (br. s, C^5, Pip), 26.2 (br. s, C^3, NC_5H_{10}), 25.8 (br. s, C^4, NC_5H_{10}) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ = 26.9 (s) ppm. $^{11}B\{^1H\}$ NMR (96.3 MHz, C_6D_6): δ = 40 (br. s) ppm. $C_{41}H_{76}BBr_2NP_2Pd$ (922.04): calcd. C 53.41, H 8.31, N 1.63; found C 54.60, H 8.27, N 1.74.

***trans*-[$(Cy_3P)_2Pd(Br)\{B(Br)Mes\}$] (5):** Br_2BMes (0.024 g, 0.083 mmol) was dissolved in a pale yellow solution of [$Pd(PCy_3)_2$] (0.055 g, 0.083 mmol) in benzene (0.5 mL), and the solution turned increasingly red. After 1 h the product signal reached a maximum and the solvent was removed in vacuo to give **5** (0.060 g, 77% conversion as determined by NMR spectroscopy) as a crude orange product. Further purification failed as the product decomposed quickly in solution. After 12 h no product peak was detectable in the ^{31}P NMR spectra. ^1H NMR (400.1 MHz, C_6D_6): δ = 6.55 (m, 2 H, CH_{arom}), 4.05 (br. s, *o*-CH_3), 3.01 (br. s, *o*-CH_3), 2.79–2.71 (m, 6 H, Cy), 2.50–2.44 (m, 6 H, Cy), 2.25–2.10 (m, 6 H, Cy), 2.04 (s, *p*-CH_3), 1.93–1.63 (m, 36 H, Cy), 1.36–1.00 (m, 18 H, Cy) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ = 148.3 (s, *o*-C, Mes), 143.6 (s, *o*-C, Mes), 141.2 (s, *p*-C, Mes), 132.4 (s, *m*-C, Mes), 130.8 (s, *m*-C, Mes), 36.3 (vt, C^1, Cy), 31.5 (m, C^3, C^5, Cy), 31.3 (*o*-CH_3, signal overlapped by byproduct), 30.3 (m, *o*-CH_3), 28.5 (m, C^2, C^6, Cy), 27.4 (s, C^4, Cy), 21.5 (s, *p*-CH_3) ppm. $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6): δ = 18.3 (s) ppm. $^{11}B\{^1H\}$ NMR (96.3 MHz, C_6D_6): δ = 89 (br. s) ppm. $C_{45}H_{68}BBr_2P_2Pd$ (956.39): calcd. C 56.51, H 8.11; found C 55.47, H 7.94.

Crystal Structure Determination: The structural data of **2** and **3** (Table 2) were collected with an X8Apex diffractometer with multilayer mirror monochromated Mo-K_α radiation and a D8Apex diffractometer with graphite monochromated Mo-K_α radiation,

Table 2. Crystal data and refinement parameters for **2** and **3**.

Compound	**2**	**3**
Empirical formula	$C_{50}H_{88}BBrO_3P_2Pd$	$C_{38}H_{72}BBr_2NP_2Pd$
Formula weight [g mol^{-1}]	996.26	881.94
Temperature [K]	173(2)	100(2)
Radiation, λ [Å]	Mo-K_α 0.71073	Mo-K_α 0.71073
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
Unit cell dimensions		
a [Å]	9.5872(6)	11.110(2)
b [Å]	18.9497(13)	29.432(6)
c [Å]	27.9300(19)	12.426(3)
α [°]	90	90
β [°]	90	94.12(3)
γ [°]	90	90
Volume [Å^3]	5074.2(6)	4052.6(14)
Z	4	4
Calculated density [mg m^{-3}]	1.304	1.445
Absorption coefficient [mm^{-1}]	1.255	2.535
F(000)	2112	1832
Theta range for collection	1.30 to 26.11°	1.38 to 26.46°
Reflections collected	87875	96922
Independent reflections	10071	8342
Refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2
Data/parameters/restrains	10071/536/33	8342/452/53
Goodness-of-fit on F^2	1.134	1.456
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0417, wR^2 = 0.0947	R_1 = 0.0487, wR^2 = 0.1210
R indices (all data)	R_1 = 0.0450, wR^2 = 0.0964	R_1 = 0.0501, wR^2 = 0.1214

respectively. The structures were solved by direct methods, refined with the SHELX software package[17] and expanded by using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized position and were included in structure factor calculations. Both structures show a partial disorder of the main residue.

CCDC-670175 (**2**) and -670176 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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