2636 *Organometallics* **1990**, *9*, 2636–2638

Novel Phosphido-Bridged Cations $[M_2(CO)_8(\mu\text{-}PPh_2)]BF_4$ (M = Fe, Ru): Synthesis, Reactivity, and X-ray Structure of an Isoelectronic and Structural Analogue of $Ru_2(CO)_9$

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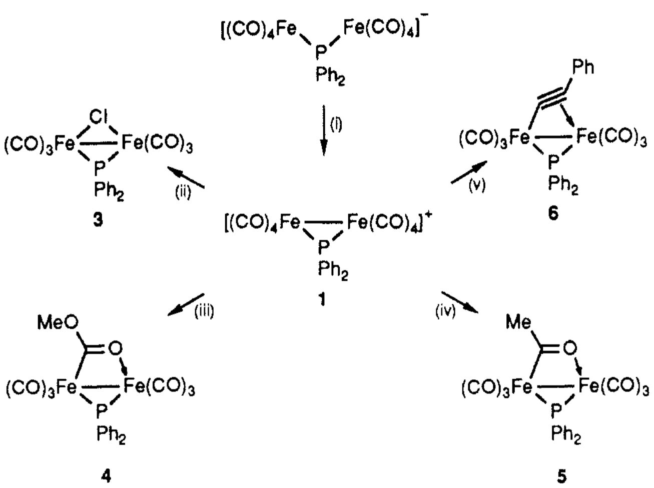
Summary: The cationic 34-electron phosphido-bridged binuclear complexes $[M_2(CO)_8(PPh_2)]BF_4$ (**1**, M = Fe; **2**, M = Ru) have been synthesized and their electrophilic reactivities explored. An X-ray analysis of **2** has revealed it to be a structural analogue of the isoelectronic but incompletely characterized $Ru_2(CO)_9$.

Extensive and fundamentally significant chemistry of μ-PPh_2 organometallics has developed over the past decade, including 34- and 36-electron neutral[1,2] species and anions,[1,3] as well as 33-electron radicals.[1] Cationic phosphido-bridged compounds are rare, however, and their systematic synthesis and potential reactivity have not been explored. We report herein the synthesis of the cationic complexes $[M_2(CO)_8(PPh_2)]BF_4$ (1, M = Fe; 2, M = Ru) and the structural characterization of the ruthenium derivative, an isoelectronic and structural analogue of $Ru_2(CO)_9$.

Complex 1 was prepared in 85% yield via the oxidation of the readily available anion $[Na(THF)_{1.5}][Fe_2(CO)_8(PPh_2)]$[4] (5.10 g, 7.83 mmol) with triphenylmethyl tetrafluoroborate (6.20 g, 18.78 mmol) in CH_2Cl_2 (80 mL) under an atmosphere of CO (Scheme I). The solvent of crystallization readily evaporated on filtration and drying and could be completely removed in vacuo to yield 1 as a straw yellow powder (4.06 g, 6.69 mmol, 85%).[5] Solutions of 1 are rapidly decomposed in air. The solid is slowly attacked by air but is stable indefinitely under an atmosphere of nitrogen.

Scheme I[a]



[a] Legend: (i) CPh_3BF_4, CH_2Cl_2, CO; (ii) NEt_4Cl, CH_2Cl_2; (iii) NaOMe, THF, −20 °C; (iv) $Li[Cu(CN)(CH_3)]$, Et_2O, −78 °C; (v) $Li[Cu(CN)(CCPh)]$, Et_2O, −78 °C.

Complex 1 shows enhanced susceptibility to nucleophilic attack with inorganic ions and complex carbanions under mild conditions (Scheme I). Addition of NEt_4Cl (0.111 g, 0.67 mmol) to 1 (0.400 g, 0.658 mmol) suspended in CH_2Cl_2 (5 mL) resulted in vigorous gas evolution, dissolution of the carbonyl, and a color change to deep red. After 10 min the solvent was evaporated, the mixture was extracted with hexane, and the extract filtered. Concentration of the filtrate to 5 mL and storage at −10 °C yielded bright red crystals of the μ-halide complex 3[6] (0.218 g, 0.436 mmol, 66%). Addition of 1 equiv of NaOMe (380 μL, 0.87 M in THF, 0.330 mmol) to a suspension of 1 (0.200 g, 0.330 mmol) in THF (5 mL) gave, in a similarly vigorous reaction, the new alkoxyacyl complex 4[7] (0.085 g, 0.163 mmol, 50%). Attempted reaction of 1 with lithium and magnesium alkyls led to intractable mixtures, but organolithium

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(5) 1: ν_{CO} (CD_2Cl_2) 2140 (w), 2097 (s), 2066 (s), 2047 (w) cm^{-1}; ^1H NMR (CD_2Cl_2, 200.00 MHz, 298 K) δ 7.0–7.8 (m, C_6H_5); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 81.02 MHz, 298 K) δ 195.87 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 50.32 MHz, 298 K) δ 215 (br, CO), 137.63 (d, $^1J_{PC}$ = 35.70 Hz, C_6H_5, ipso), 133.27 (s, C_6H_5, para), 132.20 (d, $^2J_{PC}$ = 10.31 Hz, C_6H_5, ortho), 130.48 (d, $^3J_{PC}$ = 11.61 Hz, C_6H_5, meta). Anal. Calcd for $C_{20}H_{10}O_8BF_4PFe_2$: C, 39.52; H, 1.66. Found: C, 39.19; H, 2.02. A full description of the synthesis of 1 is provided in the supplementary material.

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(7) 4: ν_{CO} (C_6H_{14}) 2071 (s), 2031 (vs), 2004 (s), 1991 (m), 1980 (m), 1973 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, 298 K) δ 7.2–7.8 (m, C_6H_5, 10), 3.05 (s, OCH_3, 3); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.9 MHz, 298 K) δ 175.15 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz, 298 K) δ 226.25 (d, $^2J_{PC}$ = 28.7 Hz, O=$COCH_3$), 210.24 (s, CO), 138.06 (d, $^2J_{PC}$ = 36.2 Hz, C_6H_5, ipso), 136.42 (d, $^2J_{PC}$ = 26.2 Hz, C_6H_5, ipso), 133.32 (d, $^2J_{PC}$ = 8.7 Hz, C_6H_5, ortho), 130.24 (s, C_6H_5, para), 129.70 (s, C_6H_5, para), 128.6 (d, $^3J_{PC}$ = 9.4 Hz, C_6H_5, meta), 128.25 (d, $^3J_{PC}$ = 9.1 Hz, C_6H_5, meta), 53.49 (s, O=$COCH_3$). Anal. Calcd for $C_{20}H_{13}O_8PFe_2$: C, 45.34; H, 2.50. Found: C, 44.91; H, 2.51. A $P(OMe)_3$ derivative of 4, obtained via treatment of 3 with NaOMe and $P(OMe)_3$, has been fully characterized by X-ray diffraction: Fortier, S.; Dhatt, I. S.; MacLaughlin, S. A. Unpublished results.

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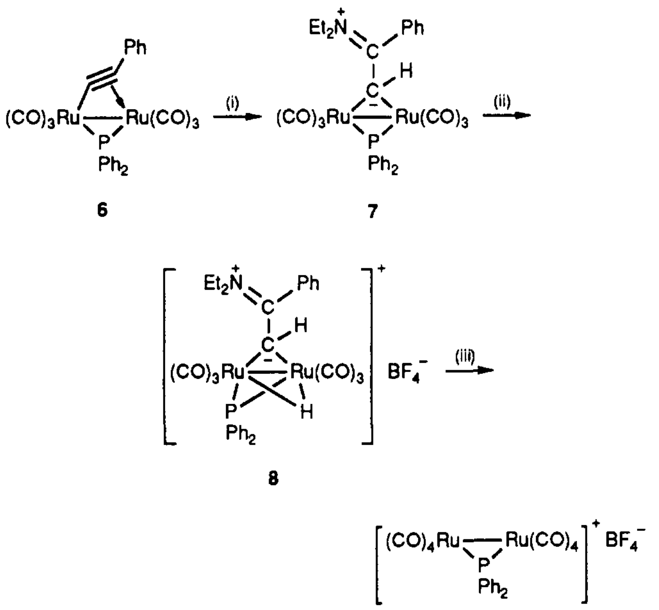
Scheme II[a]



[a] Legend: (i) Et_2NH, C_6H_{14}; (ii) $HBF_4{\cdot}Et_2O$, CH_2Cl_2, -78 °C; (iii) CO, 24 h, $ClCH_2CH_2Cl$, 25 °C.

cyanocuprates reacted smoothly. Addition of $Li[Cu(CN)(CH_3)]$ (0.23 M in THF, 0.72 mL, 0.165 mmol) to a suspension of 1 (0.100 g, 0.165 mmol) in Et_2O (10 mL) at -78 °C, followed by warming to room temperature overnight, gave the new acyl 5.[8] After evaporation of solvent, extraction with hexane, and filtration, a crystalline sample was obtained at -10 °C (0.050 g, 0.098 mmol, 60%).

Similarly, reaction with $Li[Cu(CN)(C{\equiv}CPh)]$ yielded the well-known μ-σ^1-η^1,η^2-alkynyl complex 6 (M = Fe).[9a] These cuprate reactions may thus offer an attractive and systematic route to μ-acyl and μ-hydrocarbyl complexes.

The synthetic route to 2 (Scheme II) involves the generation of the zwitterionic alkylidene complex 7 via addition of diethylamine to the triple bond of the μ-σ-η^1,η^2-alkynyl complex 6 (M = Ru).[9b] Protonation of the metal–metal bond of 7 (0.448 g, 0.614 mmol) with excess $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 (6 mL) at -78 °C gave 8[10] (0.371 g, 0.411 mmol, 67%). Reductive elimination of hydride and alkylidene from 8 (0.15 g, 0.166 mmol) in $ClCH_2CH_2Cl$ (20 mL) in the presence of CO (48 °C, 24 h) afforded 2 (0.058 g, 0.083 mmol, 50%), which crystallized as pale yellow crystals from a 1,2-dichloroethane/hexane mixture.[11] A single-crystal X-ray diffraction study of 2[12] revealed full details of the molecular structure (Figure 1). There are

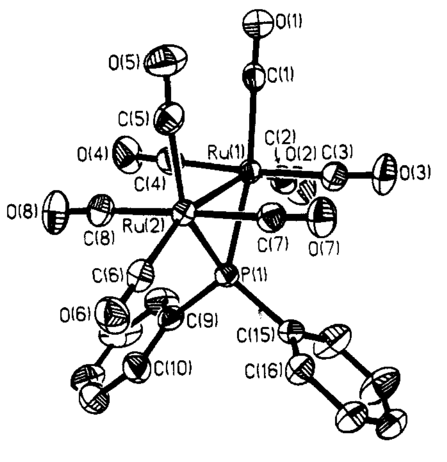


Figure 1. ORTEP drawing of $[Ru_2(CO)_8(\mu\text{-}PPh_2)]BF_4$ (2; molecule A, BF_4^- omitted). Thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths and angles: Ru(1)–Ru(2) = 2.888 (1), 2.885 (1) Å; Ru(1)–P(1) = 2.350 (1), 2.346 (1) Å; Ru(2)–P(1) = 2.340 (1), 2.349 (1) Å; Ru(1)–P(1)–Ru(2) = 76.0 (1), 75.8 (1)°.

two independent but essentially identical molecules in the asymmetric unit, with each cation having pseudo-2-fold symmetry. The ruthenium atoms are linked by a short metal–metal bond (Ru(1)–Ru(2) = 2.888 (1), 2.885 (1) Å) and a single PPh_2 bridge (Ru(1)–P–Ru(2) = 76.0 (1), 75.8 (1)°). As a 34-electron species with eight terminal carbonyls and a single bridging ligand, 2 is isoelectronic with and closely related to $Ru_2(CO)_9$,[13] an unstable and incompletely characterized molecule whose structure may, like that of $Os_2(CO)_9$,[13] contain only one bridging carbonyl. In sharp contrast, the isoelectronic dianion $Ru_2(CO)_8^{2-}$ has a non-carbonyl-bridged structure in which the two $[Ru(CO)_4]$ fragments have trigonal-bipyramidal and square-pyramidal stereochemistries in the solid state.[14] The cation does, however, bear a close structural resemblance to the 34-electron anion $[Mn_2(CO)_8(\mu\text{-}PPh_2)]^-$ described by Mays et al.[3b] The isolobal connection

$$Ru(CO)_4 \longleftrightarrow PPh_2^+$$

illustrates the structural relationship between 2 and the carbonyls $M_3(CO)_{12}$ (M = Ru, Os).

The ^{13}C NMR spectra of 1 and 2 exhibit a single set of four phenyl resonances and, for 2, three distinct carbonyl resonances at 191.1, 188.3, and 186.6 ppm in the ratios

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(8) 5: ν_{CO} (C_6H_{14}) 2069 (s), 2026 (vs), 2002 (s), 1988 (m), 1982 (w), 1977 (m) cm^{-1}: ^1H NMR ($CDCl_3$, 400 MHz, 298 K) δ 7.2–8.0 (m, C_6H_5, 10), 2.0 (s, $O{=}CCH_3$, 3); $^{31}P\{^1H\}$ NMR $CDCl_3$, 161.9 MHz, 298 K) δ 183.4 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz, 298 K) δ 300.9 (d, $^2J_{PC}$ = 23.3 Hz, $O{=}CCH_3$), 212.3 (s, CO), 211.9 (d, $^2J_{PC}$ = 23.3 Hz, CO), 210.5 (d, $^2J_{PC}$ = 14.4 Hz, CO), 138.5 (d, $^2J_{PC}$ = 24.4 Hz, C_6H_5, ipso), 133.5 (d, $^2J_{PC}$ = 8.2 Hz, C_6H_5, ortho), 133.2 (d, $^2J_{PC}$ = 8.4 Hz, C_6H_5, ortho), 130.2 (s, C_6H_5, para), 129.8 (s, C_6H_5, para), 128.6 (d, $^3J_{PC}$ = 11.9 Hz, C_6H_5, meta), 128.5 (d, $^3J_{PC}$ = 11.4 Hz, C_6H_5, meta), 47.6 (s, $CH_3C{=}O$). Anal. Calcd for $C_{20}H_{13}O_7PFe_2$: C, 47.29; H, 2.58. Found: C, 47.11; H, 2.23.

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(11) 2: ν_{CO} (CH_2Cl_2): 2152 (w), 2119 (s), 2099 (w), 2076 (vs), 2052 (w) cm^{-1}; ^1H NMR (CD_2Cl_2, 200.00 MHz, 298 K) δ 7.67–7.58 (m, C_6H_5); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 81.02 MHz, 298 K) δ 157.0 (s); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 50.32 MHz, 298 K) δ 191.1 (d, $^2J_{PC}$ = 12.0 Hz, CO_{ax}), 188.3 (d, $^2J_{PC}$ = 50.6 Hz, CO_{eq}), 186.6 (d, $^2J_{PC}$ = 12.0 Hz, CO_{eq}), 137.63 (d, $^1J_{PC}$ = 35.70 Hz, C_6H_5, ipso), 133.27 (s, C_6H_5, para), 132.20 (d, $^2J_{PC}$ = 10.31 Hz, C_6H_5, ortho), 130.48 (d, $^3J_{PC}$ = 11.61 Hz, C_6H_5, meta). Anal. Calcd for $C_{20}H_{10}BF_4O_8PRu_2$: C, 34.41; H, 1.44. Found: C, 34.03; H, 1.32.

(12) Crystal data for 2: $C_{20}H_{10}BF_4O_8PRu_2$, M_r = 698.22, monoclinic, space group $P2_1/n$, a = 14.765 (3) Å, b = 16.900 (2) Å, c = 19.999 (3) Å, β = 92.81 (1)°, V = 4984 (1) Å^3, Z = 8, T = 200 K, D_c = 1.861 g cm^{-3}, $F(000)$ = 2704, λ = 0.71073 Å, μ(Mo Kα) = 13.22 cm^{-1}. Intensity data were collected on a crystal of dimensions 0.24 × 0.26 × 0.29 mm mounted on a Nicolet R3M diffractometer, by the ω-scan technique ($2\theta < 50°$). From 8773 measured data, 7095 with $I \geq 3\sigma(I)$ were considered observed. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares to R and R_w values of 0.030 and 0.032, respectively.

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2:1:1, in keeping with effective C_{2v} symmetry. The ν(CO) IR spectra are closely similar, exhibiting high-frequency bands at 2139 and 2154 cm^{-1} for **1** and **2**, respectively, which are among the highest reported for group VIII metal carbonyls.

The isolation and characterization of the singly bridged cationic complexes **1** and **2** offer an opportunity to probe a number of fundamental aspects of the chemistry of binuclear phosphido complexes. Given their enhanced susceptibility to nucleophilic attack, they may serve as simple models for the examination of reaction mechanisms leading to bridge cleavage[3a,e15] and/or ligand substitution.[1,2a,b] In addition, they should be useful synthons for cluster chemistry. We are currently exploring these possibilities.

Acknowledgment. We acknowledge the support of the Natural Sciences and Engineering Research Council of Canada.

Supplementary Material Available: A full description of the synthesis of **1** and listings of X-ray crystal data, atomic positions, anisotropic thermal parameters, and bond lengths and angles for **2** (11 pages); a listing of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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Polyhedral Aluminosilsesquioxanes as Models for Aluminosilicates: Unique Synthesis of Anionic Al/Si/O Frameworks

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Summary: An efficient procedure for the synthesis of polyhedral aluminosilsesquioxanes has been developed and applied to the synthesis of **7**, an anionic aluminosilsesquioxane that is formally derived from two corner-sharing D4R subunits of Linde type A zeolite. The salient feature of this procedure is the use of tetramethylstibonium siloxides as mild sources of siloxide anions. Tetramethylstibonium siloxides can be prepared from silanols by using standard means or from the oxidation of hydridosilsesquioxanes with Me_3NO.

We recently reported the synthesis of **2**, an excellent latent source of **3** and a versatile precursor for the syntheses of polyhedral aluminosilsesquioxanes.[1a] In this paper we describe an interesting procedure for the synthesis of anionic aluminosilsesquioxanes. The utility of this procedure, which exploits a unique property of tetramethylstibonium siloxides (and alkoxides), is demonstrated by synthesizing **7**, an anionic aluminosilsesquioxane that is formally derived from two corner-sharing D4R subunits of Linde type A zeolite.

The most obvious approach to anionic aluminosilsesquioxanes, the reaction of **2** with alkali-metal siloxides (e.g., $MOSiMe_3$, M = Li, Na, K), produces complex mixtures of intractable products. Even in nonpolar media, where strong contact ion pairing greatly reduces anion nucleophilicities, alkali-metal siloxides (and alkoxides) quickly destroy most silsesquioxane frameworks. The nucleophilicity of siloxide anions can, however, be tempered by using tetramethylstibonium siloxides (e.g., $Me_4SbOSiMe_3$), which are actually hydrocarbon-soluble molecular species with five-coordinate antimony centers. These interesting "pseudosalts" are excellent sources of siloxide anions under very mild conditions.[2]

The reaction[3] of **2** with $Me_4SbOSiMe_3$[2b] in C_6H_6 (80 °C, 12 h) affords a virtually quantitative yield of **4**, which was easily identified on the basis of ^1H, ^{13}C, and ^{29}Si NMR spectral data. Both the ^{29}Si NMR spectrum and the methine region of the ^{13}C NMR spectrum of **4** exhibit three resonances with the expected relative intensities of 3:3:1, while the ^{13}C NMR spectrum exhibited a singlet resonance (δ −0.72) characteristic of the four-coordinate $[Me_4Sb]^+$ ion.[4]

The thermodynamic stability of **4** and efficiency of its synthesis suggested that a variety of interesting aluminosilsesquioxanes (e.g., **7**) could be synthesized from **2**, if a convenient source of anhydrous tetramethylstibonium siloxides and/or silicates could be discovered. Unfortunately, the usual methods[5] for synthesizing stibonium si-

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[1] (a) Feher, F. J.; Budzichowski, T. A.; Weller, K. J. *J. Am. Chem. Soc.* **1989**, *111*, 7288–9. (b) Feher, F. J.; Newman, D. A.; Walzer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 1741–8.

[2] (a) Schmidbauer, H.; Weidlein, J. Z.; Mitschke, K.-H. *Ber.* **1969**, *102*, 4136–46. (b) Schmidbaur, H.; Arnold, H.-S.; Beinhofer, E. *Ber.* **1964**, *97*, 449–66. (c) Eberwein, B. B.; Ott, R.; Weidlein, J. *Z. Anorg. Allg. Chem.* **1977**, *431*, 95–104. (d) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 201–11.

[3] In a typical reaction, $Me_4SbOSiMe_3$ (1.00 mmol) was added to a solution of **2** (576 mg, 0.288 mM) in benzene. The solution was refluxed for 12 h and then evaporated (25 °C, 0.1 mTorr) to give **4** in virtually quantitative yield (by ^1H and ^{13}C NMR spectroscopy). Analytically pure **4** was obtained by recrystallization from C_6H_6/hexane. Spectroscopic and analytical data for **4** are as follows. ^1H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ 2.26–2.18 (m, 14 H), 1.90–1.67 (complex, m, 35 H), 1.41–1.22 (complex m, 21 H), 1.10–1.06 (complex m, 4 H), 1.05 (s, 12 H), 0.96–0.85 (m, 3 H), 0.327 (s, 9 H). $^{13}C\{^1H\}$ NMR (125.03 MHz, C_6D_6, 25 °C): δ 28.62, 28.53, 28.47, 28.36, 28.21, 28.14, 28.04, 27.90, 27.79, 27.62, 27.48 (CH_2), 25.93, 24.72, 24.28 (3:3:1 for CH), 3.82 ($SiMe_3$), −0.72 ($SbMe_4$). $^{29}Si\{^1H\}$ NMR (99.3 MHz, C_6D_6, 25 °C): δ 0.035, −66.59, −68.35, −69.52 (1:3:1:3). Anal. Calcd (found) for $C_{49}H_{98}AlO_{13}Si_8Sb$: C, 46.39 (46.54); H, 7.78 (8.07). Mp: >400 °C.

[4] In C_6D_6 at 25 °C, resonances for the Me_4Sb groups in five-coordinated complexes (e.g., $Me_4SbOSiMe_3$, $Me_4SbOCMe_3$, Me_5Sb) typically occur downfield from 10 ppm in ^{13}C NMR spectra. Resonances for the Me_4Sb groups in four-coordinate complexes (e.g., $[Me_4Sb][Al(OSiMe_3)_4]$) typically occur upfield from 0 ppm.

[5] The two most common methods for synthesizing stibonium siloxides are the reactions of alkali-metal siloxides with $[Me_4Sb]Cl$[2b] and the reactions of silanols with Me_5Sb.[2a,c]

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