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Some chiral alkyne-cobalt complexes

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Abstract

The trimethyl phosphite substituted pentacarbonylpropargyldicobalt cation, $[(CH{\equiv}CCH_2)Co_2(CO)_5L]^+$ [L = $P(OMe)_3$], is significantly more stable than its phosphine analogues (L = PPh_3, PBu_3), and has been converted to a series of ethers, $(CH{\equiv}CCH_2OR)Co_2(CO)_5L$. Reaction of the (cholesteryl propargyl ether)hexacarbonyldicobalt complex with trimethyl phosphite proceeds without stereoselectivity, and the product suffers metal–carbon rather than oxygen–carbon cleavage on treatment with acid.

Introduction

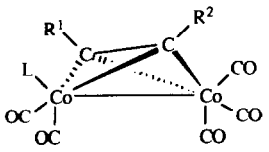
Acetylene complexes of the type **1** are chiral provided that $R^1 \neq R^2$ and L ≠ CO. We have previously used this fact [1] in some asymmetric Khand reactions relying on the use of a homochiral phosphine ligand (L). Our choice of "glyphos" for this ligand led to very high enantioselectivity in reaction with norbornene, but the lower reactivity of other alkenes examined, necessitating longer reaction time, led to substantially poorer results due to the easy loss of phosphine ligand and hence interconversion of the two diastereoisomeric forms of the starting complex.

We hoped to avoid the need for asymmetric phosphines altogether, and to make complexes available which would be useful for other reactions as well as further asymmetric Khand reactions by proceeding via the "Nicholas cations" of the type **2** [2]. If these proved to be sufficiently readily accessible in homochiral form and sufficiently optically stable, they could in principle be used *inter alia* for resolution of alcohols or amines.

The idea of resolving such cations via the corresponding ethers of alcohols from the natural chiral pool also underlies the recently published work of D'Agostino, Frampton and McGlinchey [3]. The appearance of this paper prompts our decision to record our own more limited findings at this stage, largely because the combined results discourage further pursuit of our immediate objectives.

Results and discussion

Whereas D'Agostino et al. [3] converted the propargyl alcohol complex **3a** into its bornyl and menthyl ethers and then replaced carbon monoxide by phosphines (a



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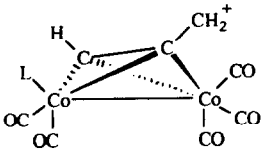

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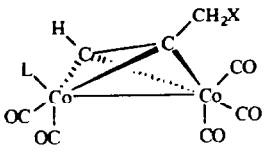

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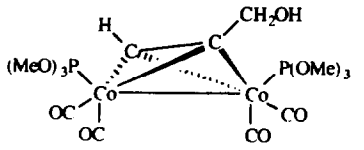
a. L=CO; X=OH
b. L=PPh_3; X=OH
c. L=PBu_3; X=OH
d. L=$P(OMe)_3$; X=OH
e. L=PPh_3; X=$OCH_2CH{=}CH_2$
f. L=CO; X=$OCH_2CH{=}CH_2$
g. L=$P(OMe)_3$; X=$OCH_2CH{=}CH_2$
h. L=$P(OMe)_3$; X=OBu^n
i. L=$P(OMe)_3$; X=OCH_2Ph
j. L=$P(OMe)_3$; X=OCHMeEt
k. L=$P(OMe)_3$; X=OBu^t
l. L=$P(OMe)_3$; X=$N(CH_2)_5$

reaction which proceeded with little or no enantioselectivity) we initially attempted the reverse sequence. Thus, complex **3a** was converted into the triphenyl- (**3b**) and tributylphosphine complexes (**3c**), but attempts to convert these via the cations **2** into ethers of borneol or quinine failed. Even with simple alcohols, pure complexes could not be obtained, apparently because of lability of the phosphine ligand. Thus, whereas the triphenylphosphine complex **3b** yielded the fluoroborate of the cation **2** (L = PPh_3) as a red powder which, on one occasion gave with allyl alcohol, a product characterised by mass spectrum as the expected ether **3e**, a repeat experiment gave mixtures, or even pure hexacarbonyl complex **3f**. Some nucleophiles (alcohols, amines) appeared not to react with the cations, so that the bis(hexacarbonyldicobalt) complex of dipropargyl ether became the chief product on workup.

The trimethyl phosphite complex **3d** is significantly more stable than its phosphine analogues, and could be prepared in good yield and separated chromatographically from the by-product, the bis-phosphite complex **4**. The cation **2** [L = $P(OMe)_3$] generated from this alcohol **3d** with fluoroboric acid, although not isolated as a pure salt, reacted with three primary alcohols (allyl, benzyl, and butyl) and a secondary (2-butyl), and a tertiary alcohol (tert-butyl) to give moderate to good yields of the corresponding ethers **3g–k**, and also with piperidine, although the amine **31** was not obtained completely pure. Yet, reaction with borneol or its 2-*endo*-methyl derivative (from D-camphor + methylmagnesium iodide) failed to give the desired ethers under conditions rather similar to those successfully employed by D'Agostino et al. [3] with the hexacarbonyl cation **2** (L = CO).

We turned finally to the use of a preformed homochiral propargyl ether **5**, which we obtained by prolongued treatment of cholesterol with potassium hydride, followed by propargyl bromide. This ether **5** reacted smoothly with octacarbonyldicobalt to give the expected complex **6a**. Treatment of the latter with trimethyl phosphite in toluene, promoted by ultrasound, gave a mixture of the required phosphite complex **6b** and the corresponding bis-phosphite tetracarbonyldicobalt complex. These were separated chromatographically, but although



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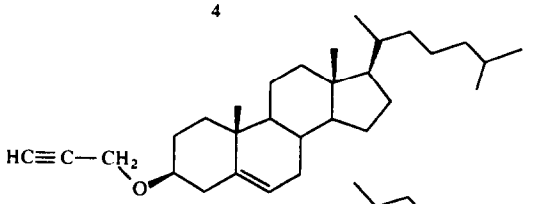

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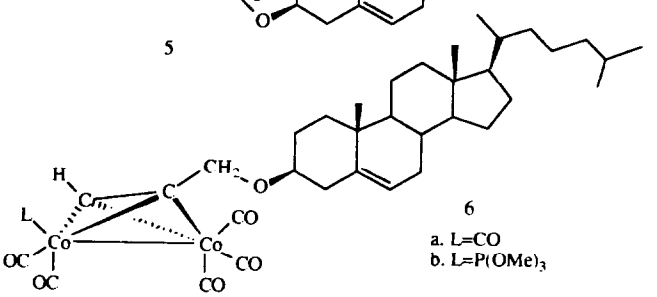

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a. L=CO
b. L=P(OMe)3

the former **6b** appeared homogeneous by TLC, its ^{1}H NMR spectrum showed a double doublet for the OCH_3 protons of the phosphite ligand, corresponding to a ~ 1:1 mixture of the two diastereoisomers. This disappointing lack of stereoselectivity is entirely consistent with the findings of the Canadian workers [3]. Equally disappointing was the finding that fluoroboric acid, far from causing cleavage of the ether to the cation **2** [L = $P(OMe)_3$], caused cleavage of the alkyne-cobalt bonds to regenerate the metal-free propargyl ether, **5**. If this behaviour is general, then even if single diastereoisomers were obtained, ethers such as complex **6b** could not serve the original purpose of our study.

The new complexes are described in the experimental section.

Experimental

All reactions were carried out under nitrogen.

*The propargyl alcohol complexes **3a–3d***

(a) The hexacarbonyl complex **3a** was obtained (80–96%) by a published method [4] and had m.p. 52–53 °C.

(b) Following R. Eder [5], triphenylphosphine (0.38 g, 1.46 mmol) was added to a solution of the complex **3a** (0.50 g, 1.46 mmol) in hexane (40 ml) under nitrogen and the mixture stirred at 55 °C for 1 h. The products were chromatographed on neutral alumina and eluted with ether/n-hexane (1:4). After elution of unchanged phosphine (60 mg) and hexacarbonyl complex **3a** (139 mg), the pentacarbonyl(triphenylphosphine) complex **3b** (0.428 g, 70%) was isolated as wine-coloured crystals. IR: ν_{max}(CO) (light petroleum) 2070, 2008, 2000, 1976 cm^{-1}.

(c) Tri-n-butylphosphine (4.89 g, 2.42 mmol) was similarly added to the hexacarbonyl complex **3a** (8.29 g, 2.42 mmol) in hexane (100 ml) and the mixture stirred at 50–60 °C for 1.5 h. Chromatography with n-hexane as eluant gave unchanged phosphine (850 mg) followed first by the bis-phosphine-substituted complex (220 mg, 3%) and then by the desired product **3c**, as a dark red oil (9.18 g, 89%). IR: ν_{max} 3330, 2955, 2930, 2900, 2870, 2045, 2000–1940 cm^{-1}, ^1H NMR ($CDCl_3$): δ 5.35 (1H, d, HC≡); 4.66 (2H, br d, CH_2O); 1.70–1.37 (18H, m, CH_2); 0.96 (9H, t, CH_3). Found: C, 46.8; H, 6.2. $C_{20}H_{31}Co_2O_6P$ calc.: C, 46.5; H, 6.05%.

(d) Application of the above method to trimethyl phosphite gave only low yields of the complex **3d**. This was best obtained as follows. Trimethyl phosphite (7.26 g, 58.5 mmol) was added to a solution of the hexacarbonyl complex **3a** (20 g, 58.5 mmol) in dry, redistilled toluene (350 ml) under argon. The mixture was irradiated with ultrasound in a laboratory cleaning bath for 7 h, then filtered through kieselguhr and the solvent removed in a rotary evaporator. Chromatography on neutral alumina, with n-hexane as eluant, gave the unchanged hexacarbonyl complex (2 g) followed by product **3d** (19.78 g, 90%) and finally the bis-phosphite complex **4** (0.52 g, 3%). The complex **3d** is a deep red oil. IR: ν_{max} 3419, 3000, 2953, 2850, 2100, 2066, 2040–1960, 1020 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.60 (1H, dt, HC≡); 4.70 (2H, m, CH_2); 3.63 (9H, d, OMe), 2.17 (1H, s, OH). Found: C, 30.5; H, 2.8. $C_{11}H_{13}Co_2O_9P$ calc.: C, 30.2; H, 3.0%.

Tetrafluoroborate of the cation 2d

Complex **3d** (1.73 g, 3.95 mmol) was dissolved in propionic anhydride (5 ml) and the solution was cooled to −45 °C. Tetrafluoroboric acid etherate (2.77 g, 3.26 ml, 17.1 mmol) was then added dropwise with vigorous stirring which was continued for a further 30 min at the same temperature. Diethyl ether (100 ml) was then added and the mixture kept at ca. −100 °C for 2 h. The supernatant liquid was then decanted, more cold ether was added, and after further cooling the crystalline fluoroborate of the cation **2d** (1.89 g, 94%) was filtered off and used without further characterisation.

The allyl ether 3g

To the preceding salt (1.89 g, 3.7 mmol) and sodium hydrogen carbonate (1 g) in a Schlenck tube cooled to −45 °C, allyl alcohol (10 ml) was added with vigorous stirring. The mixture was allowed to warm to room temperature, dry ether (50 ml) was added, and stirring continued for a further 2 h. The solution was then filtered through kieselguhr and evaporated, and the residue chromatographed on neutral alumina with ether/n-hexane (1 : 4) as eluant. This gave the ether **3g** as a dark red oil (1.06 g, 60%). IR ν_{max} 3082, 2950, 2842, 2067, 2020–1940, 1010 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.2–5.7 (1H, m, CH=); 5.57 (1H, m, HC≡); 5.3 (2H, m, CH_2=); 4.62 (2H, br s, ≡CCH_2); 4.14 (2H, m, =CHCH_2); 3.62 (9H, d, OMe). Found: C, 35.3; H, 3.8. $C_{14}H_{17}Co_2O_9P$ calc.: C, 35.2; H, 3.6%.

The n-butyl ether 3h

As described by Smit et al. [6], tetrafluoroboric acid-dimethyl etherate (0.89 g, 6.6 mmol) was added at −78 °C to a solution of the propargyl alcohol complex **3d** (1.45 g, 3.3 mmol) in dichloromethane (10 ml). After 15 min stirring 1-butanol (0.978 g, 13.2 mmol) was slowly injected at −78 °C through a subaseal. Stirring at

this temperature was maintained for a further 2 h and saturated aqueous sodium hydrogen carbonate (10 ml) was then added. The mixture was allowed to warm to room temperature with stirring, then extracted with ether. The dried ($MgSO_4$) extract was evaporated and the residue chromatographed on neutral alumina with ether/n-hexane (1:4) as eluant. The main fraction yielded the ether **3h** (1.17 g, 72%) as a dark red oil. IR: ν_{max} 3950, 2870, 2840, 2090, 2075, 2040–1950, 1100, 1025 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.55 (1H, d, HC≡); 4.57 (2H, br s, ≡CCH_2); 3.62 (11H, d + m, OMe + OCH_2CH_2); 1.52 (4H, m, $CH_2CH_2CH_3$); 0.92 (3H, t, CH_3CH_2). Found: C, 36.4; H, 4.2; P, 6.45. $C_{15}H_{21}Co_2O_9P$ calc.: C, 36.5; H, 4.3; P, 6.3%.

The benzyl ether 3i

Following a procedure similar to that used for the allyl ether **3g** the fluoroborate prepared from complex **3d** (0.6 g, 1.37 mmol) and $HBF_4 \cdot OEt_2$ (1.11 g, 1.3 ml, 6.85 mmol) was dissolved in dichloromethane (2 ml) and the solution stirred for 45 min with benzyl alcohol (0.3 g, 0.29 ml, 2.77 mmol) in the same solvent (3 ml) and sodium hydrogen carbonate (0.5 g). This reaction was incomplete, and has not been optimised. Ether/light petroleum (1:1) eluted the ether **3i** (0.221 g, 31%) as a somewhat unstable dark red oil. IR ν_{max} 3075, 3040, 3010, 2955, 2850, 2075, 2020, 2000, 1960, 1160, 1020, 747, 698 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.35 (5H, m, Ph); 5.55 (1H, dt, J(H–P) = 3.5 Hz, HC≡); 4.65 (4H, m, CH_2O); 3.57 (9H, d, J(H–P) = 12 Hz, OMe). Due to partial decomposition, a satisfactory analysis was not obtained, but the product was further characterised by its high resolution mass spectrum: *m/e* Found: 527.9429; $C_{18}H_{19}Co_2O_9P$ calc.: 527.9431; major fragment ions: $C_{17}H_{19}Co_2O_8P$ (M – CO): 499.9464 (499.9482), $C_{15}H_{19}Co_2O_6P$ (M – 3CO): 443.9582 (443.9583), $C_{14}H_{19}Co_2O_5P$ (M – 4CO): 415.9606 (415.9634), and $C_{13}H_{19}Co_2O_4P$ (M – 5CO): 387.9670 (387.9685).

The 2-butyl ether 3j

Following the procedure used for the n-butyl ether **3h**, above, a mixture of complex **3d** (0.794 g, 1.8 mmol), $HBF_4 \cdot OMe_2$ (0.485 g, 3.6 mmol), butan-2-ol (0.534 g, 7.2 mmol) and dichloromethane (4 ml) was stirred at −78 °C for 2.5 h. Chromatography, with ether/hexane (1:3) as eluant, gave the product **3j** (0.537 g, 69%) and unchanged **3d** (0.102 g). Complex **3j** is a dark red oil. IR: ν_{max} 2980, 2960, 2892, 2960, 2840, 2110, 2080, 2060–1900, 1110, 1025 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.52 (1H, m, HC≡); 4.57 (2H, m, ≡CCH_2); 3.61 (9H, dd, J(H–P) = 12 Hz, OMe); ca. 3.58 (1H, m, OCH); 1.15 (3H, dd, $CHCH_3$); 0.91 (5H, m, CH_2CH_3). Found: C, 36.6; H, 4.0. $C_{15}H_{21}Co_2O_9P$ calc.: C, 36.5; H, 4.3%.

The tert-butyl ether 3k

As described by Padmanabhan and Nicholas [7], complex **3d** (0.667 g, 1.5 mmol) was dissolved in dichloromethane (10 ml) at 0 °C and $HBF_4 \cdot OEt_2$ (1.29 g, 8 mmol) added. The mixture was stirred at 0 °C for 1 h then evaporated under high vacuum. The residual salt was redissolved in dichloromethane (5 ml), tert-butanol (2 ml) was added at 0 °C, and the mixture stirred at 0 °C for 20 min and then, after addition of $NaHCO_3$ (1 g) and $MgSO_4$ (1 g) for a further 10 min. The solution was filtered through kieselguhr and evaporated and the residue was treated with n-hexane and filtered. This left behind unchanged fluoroborate salt (0.291 g) and

gave a solution, which, on chromatography with hexane as eluant, gave the ether **3k** (0.194 g, 47%) as a dark red oil. IR: ν_{max} 2975, 2950, 2840, 2067, 2020, 2000, 1990, 1983, 1190, 1018 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.51 (1H, dt, J(H–P) = 3.5 Hz, HC≡); 4.66 (2H, m, ≡CCH_2); 3.60 (9H, d, J(H–P) = 12 Hz, OMe); 1.22 (9H, s, CCH_3). Found: C, 36.95; H, 4.2. $C_{15}H_{21}Co_2O_9P$ calc.: C, 36.5; H, 4.3%.

The N*-propargylpiperidine complex* ***3l***

To a solution in dichloromethane (10 ml) of the fluoroborate prepared from complex **3d** (0.517 g, 1.18 mmol) and $HBF_4 \cdot OEt_2$ (0.95 g, 1.12 ml, 6 mmol) piperidine (3 ml) was added at −70 °C. The mixture was stirred while warming to room temperature and then for a further 3 h. Ether and aqueous sodium hydrogen carbonate were added and the ether layer separated, dried ($MgSO_4$) and evaporated and the residue chromatographed. n-Hexane eluted the amine complex **3l** (0.2469 g, 59%) and then unchanged complex **3d** (0.155 g). **3l**: IR: ν_{max} 2930, 2865, 2782, 2745, 2065, 2020–1950, 1020 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.62 (1H, br s, HC≡); 4.00 (2H, br s, ≡CCH_2); 3.62 (9H, d, J(H–P) = 12 Hz, OMe); 2.74 (4H, m, CH_2N); 1.70 (4H, br s, CH_2CH_2N); 1.47 (2H, br s, $CH_2CH_2CH_2N$). Both the NMR spectrum and the microanalysis indicated the presence of impurity: Found: C, 38.85; H, 3.9; N, 2.7. $C_{16}H_{22}Co_2NO_8P$ calc.: C, 38.0; H, 4.4; N, 2.8%. This unstable complex was further characterised by its mass spectrum which showed no parent ion, but all the fragments expected from successive loss of CO groups: $C_{15}H_{22}Co_2NO_7P$ (M − CO): m/e 476.9771 (calc. 476.9798), $C_{14}H_{22}Co_2NO_6P$ (M − 2CO): 448.9798 (448.9849), $C_{13}H_{22}Co_2NO_5P$ (M − 3CO): 420.9879 (420.9900), $C_{12}H_{22}Co_2NO_4P$ (M − 4CO): 392.9834 (392.9951), and $C_{11}H_{22}Co_2NO_3P$ (M − 5CO): 364.9959 (365.0001).

Cholesteryl propargyl ether ***5***

Sodium hydride (4.8 g, 0.2 mol) was added to cholesterol (19.33 g, 50 mmol) in *p*-xylene (60 ml) and the mixture was heated under reflux for 24 h then cooled. Propargyl bromide (7.14 g, 60 mmol) was added and the mixture kept at 40 °C for 2 h. After addition of water, the organic layer was dried and most of the solvent removed *in vacuo*. The residue was chromatographed on neutral alumina. n-Hexane/ether (1:1) eluted the ether **5** (17.85 g, 99% based on unrecovered cholesterol) followed by cholesterol (2.85 g). The ether **5** is a yellowish waxy solid. IR: ν_{mas} 3255, 3000–2800, 2105, 1075 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.40 (1H, m, H-6); 4.21 (2H, d, ≡CCH_2); 3.40 (1H, br m, H-3); 2.39 (1H, t, HC≡); 2.2–0.6 (44H, m, all other H). Found: C, 84.6; H, 11.1. $C_{30}H_{48}O$ calc.: C, 84.8; H, 11.4%.

*Hexacarbonyl(cholesteryl propargyl ether)dicobalt (****6a****)*

Octacarbonyldicobalt (2.41 g, 7 mmol) was dissolved in hexane (50 ml) and the progargyl ether **5** (3 g, 7 mmol) in hexane (15 ml) added. The mixture was stirred for 24 h at room temperature, and the solution then filtered through kieselguhr and evaporated. The residue was chromatographed on neutral alumina, hexane eluting the complex **6a** (4.47 g, 90%), a dark red solid. IR: ν_{max} 3000–2800, 2090, 2070, 2055, 2030, 2010, 2000, 1100 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.03 (1H, br s, HC≡); 5.37 (1H, m, H-6); 4.67 (2H, br s, ≡CCH_2); 3.40 (1H, br m, H-3); 2.40–0.65 (43H, m, all other H). Found: C, 60.1; H, 6.6. $C_{36}H_{48}Co_2O_7$ calc.: C, 60.1; H, 6.8%.

*The phosphite substituted complex **6b***

As described for the preparation of complex **3d**, above, a solution of complex **6a** (4.3 g, 6 mmol), and trimethyl phosphite (1.66 g, 7.21 mmol) in toluene (70 ml) was subjected to ultrasound for 15 h. After concentration, the product was chromatographed on neutral alumina; with n-hexane as eluant the unchanged complex **6a** (0.473 g) was followed by the red crystalline complex **6b** (2.53 g, 58%) and then by the corresponding bis-phosphite complex (1.23 g, 25%). **6b**: IR: ν_{max} 2940, 2900–2840, 2070, 2020–1970, 1020 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.54 (1H, d, J(H–P) = 3.5 Hz, HC≡); 5.34 (1H, m, H-6); 4.63 (2H, d, ≡CCH_2); 3.61 (9H, dd, J(H–P) = 12 Hz, OMe); 3.48 (1H, m, H-3); 2.44–0.80 (43H, m, all other H). Found: C, 56.6; H, 7.4. $C_{38}H_{57}Co_2O_9P$ calc.: C, 56.6; H, 7.2%. The bis(trimethyl phosphite) complex: IR: ν_{max} 2940, 2862, 2840, 2062, 2040–1930, 1016 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.35 (1H, d, HC≡); 5.08 (1H, t, H-6); 4.56 (2H, s, ≡CCH_2); 3.59 (18H, m, OMe); 3.37 (1H, m, H-3); 2.40–0.80 (43H, m, all other H).

*Acid cleavage of complex **6b***

To a solution of complex **6b** (0.485 g, 0.6 mmol) in dichloromethane (3 ml), tetrafluoroboric acid dimethyl etherate (0.335 g, 2.5 mmol) was added very slowly at 0 °C. The mixture was then allowed to warm to room temperature and stirred for 48 h. After addition of saturated aqueous $NaHCO_3$ and extraction with ether, the dried ($MgSO_4$) extract was filtered through kieselguhr and evaporated to leave almost pure cholesteryl propargyl ether **5** (0.25 g, 98%), identical with the sample described above.

Acknowledgement

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