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Synthesis and catalytic activity of histidine-based NHC ruthenium complexes

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Experimental Procedures

General comments. N_α -Acetyl-L-histidine^{S1} and complexes **7a**^{S2}, and **7b**^{S3} were prepared according to literature procedures. All other reagents are commercially available and were used as received. Unless specified otherwise, NMR spectra were recorded at 25 °C on Bruker or Varian spectrometers at the frequencies indicated. Chemical shifts (δ in ppm, coupling constants J in Hz) were referenced to residual solvent resonances. Assignments are based on homo- and heteronuclear shift correlation spectroscopy and comparison with related compounds. Elemental analyses were performed by the Microanalytical Laboratory at University College Dublin (Ireland) and at the ETH Zürich (Switzerland).

Synthesis of 3. Thionyl chloride (17.5 mL, 240 mmol) was added dropwise to a solution of N_α -acetyl-L-histidine **2** (11.8 g, 60 mmol) in *n*-butanol (100 mL) at 0 °C. Stirring was continued at 0 °C for 6 h and then at rt for 18 h. Most of the solvent was evaporated and an aqueous solution of NH₃ was added until pH > 8. The product was extracted with CHCl₃ (5 × 50 mL). The combined organic layers were washed with H₂O (2 × 50 mL) and brine (1 × 50 mL) and dried over Na₂SO₄. The solvent was removed under reduced pressure and the resulting white solid was dried under high vacuum (13.6 g, 90 % yield).

¹H NMR (360 MHz, CDCl₃) δ 7.54 (s, 1H, C_εH), 7.32 (d, ³ J_{HH} = 7.3 Hz, 1H, N_βH), 6.78 (s, 1H, C_δH), 4.74-4.79 (m, 1H, C_αH), 4.06 (t, ³ J_{HH} = 6.5 Hz, 2H, COOCH₂), 3.03-3.14 (m, 2H, C_βH₂), 2.00 (s, 3H, CH₃CO), 1.52-1.60 (m, 2H, CH₂CH₂CH₃), 1.31 (sextet, ³ J_{HH} = 7.3 Hz, 2H, CH₂CH₃), 0.89 (t, ³ J_{HH} = 7.3 Hz, 3H, CH₂CH₃), N_{δ/ε}H not resolved; ¹³C{¹H}NMR (90 MHz, CDCl₃) δ 171.6 (C=O), 170.5 (C=O), 135.1 (C_εH), 134.2 (C_γ), 115.8 (C_δH), 65.2 (COOCH₂), 52.6 (C_αH), 30.4 (CH₂CH₂CH₃), 29.2 (C_βH₂), 23.1 (CH₃CO), 18.9 (CH₂CH₃),

13.6 (CH₂CH₃); *m/z* (HRMS, ESI⁺) found 254.1494 ([M + H]⁺), C₁₂H₂₀N₃O₃ requires 254.1499.

Synthesis of 4. To a solution of **3** (5.0 g, 20 mmol) in dry DMF (50 mL) at 0 °C under N₂ atmosphere was added NaH (55-65% in oil, 947 mg, 21.7 mmol) in small portions. After stirring the mixture at 0 °C for 1 h, a solution of 2-iodopropane (2.2 mL, 22 mmol) in dry DMF (25 mL) was added dropwise. Stirring was continued at rt for 20 h. The reaction mixture was poured into H₂O (100 mL) and extracted with CHCl₃ (6 × 70 mL). The combined organic layers were washed with KOH (1M, 1 × 50 mL), H₂O (2 × 70 mL), and brine (2 × 70 mL), dried over Na₂SO₄, and evaporated to dryness. The residual oil was purified by column chromatography (SiO₂, CHCl₃/MeOH 95:5) to give **4** as a pale yellow oil (2.95 g, 51 % yield).

¹H NMR (360 MHz, CDCl₃) δ 7.36 (br, 1H, N_βH) 7.35 (s, 1H, C_εH), 6.64 (s, 1H, C_δH), 4.65-4.70 (m, 1H, C_αH), 4.18 (septet, ³J_{HH} = 6.6 Hz, 1H, (CH₃)₂CH), 3.97 (t, ³J_{HH} = 6.7 Hz, 2H, COOCH₂), 2.98 (dd, ²J_{HH} = 14.8 Hz, ³J_{HH} = 5.7 Hz, 1H, C_βH₂), 2.88 (dd, ²J_{HH} = 14.8 Hz, ³J_{HH} = 4.8 Hz, 1H, C_βH₂), 1.93 (s, 3H, CH₃CO), 1.43-1.51 (m, 2H, CH₂CH₂CH₃), 1.36 (d, ³J_{HH} = 6.6 Hz, 6H, (CH₃)₂CH), 1.24 (sextet, ³J_{HH} = 7.3 Hz, 2H, CH₂CH₃), 0.81 (t, ³J_{HH} = 7.3 Hz, 3H, CH₂CH₃); ¹³C{¹H}NMR (90 MHz, CDCl₃) δ 171.4 (C=O), 169.8 (C=O), 137.2 (C_γ), 134.6 (C_εH), 114.1 (C_δH), 64.6 (COOCH₂), 52.3 (C_αH), 48.9 ((CH₃)₂CH), 30.3 (CH₂CH₂CH₃), 29.5 (C_βH₂), 23.37 ((CH₃)₂CH), 23.36 ((CH₃)₂CH), 22.9 (CH₃CO), 18.7 (CH₂CH₃), 13.4 (CH₂CH₃); *m/z* (HRMS, ESI⁺) found 296.1966 ([M + H]⁺), C₁₅H₂₆N₃O₃ requires 296.1969.

Synthesis of 5a. A solution of **4** (2.7 g, 9.1 mmol) and MeI (1.14 mL, 18.3 mmol) in dry toluene (100 mL) was stirred at reflux for 16 h under N₂ atmosphere. The solution was cooled to rt and the toluene was decanted off. The residue was washed with EtOAc (4 × 30 mL) and

purified by column chromatography (SiO₂, MeCN) to give the imidazolium salt **5** as a hygroscopic white solid (1.39 g, 35 % yield).

¹H NMR (360 MHz, CDCl₃) δ 9.54 (s, 1H, C_εH), 7.56 (d, ³J_{HH} = 8.0 Hz, 1H, NH), 7.44 (s, 1H, C_δH), 4.79 (ddd, ³J_{HH} = 4.5, 8.0, 8.8 Hz, 1H, C_αH), 4.66 (septet, ³J_{HH} = 6.6 Hz, 1H, (CH₃)₂CH), 4.11-4.23 (m, 2H, COOCH₂), 3.98 (s, 3H, NCH₃), 3.40 (dd, ²J_{HH} = 15.9 Hz, ³J_{HH} = 8.8 Hz, C_βH₂), 3.23 (dd, ²J_{HH} = 15.9 Hz, ³J_{HH} = 4.5 Hz, C_βH₂), 2.07 (s, 3H, CH₃CO), 1.60-1.68 (m, 2H, CH₂CH₂CH₃), 1.61 (d, ³J_{HH} = 6.6 Hz, 6H, (CH₃)₂CH), 1.32-1.42 (m, 2H, CH₂CH₃), 0.93 (t, ³J_{HH} = 7.4 Hz, 3H, CH₂CH₃); ¹³C{¹H}NMR (90 MHz, CDCl₃) δ 170.1 (C=O), 169.3 (C=O), 134.2 (C_εH), 131.1 (C_γ), 118.2 (C_δH), 65.0 (COOCH₂), 52.4 ((CH₃)₂CH), 49.6 (C_αH), 33.5 (NCH₃), 29.6 (CH₂CH₂CH₃), 24.8 (C_βH₂), 22.3 (CH₃CO + ((CH₃)₂CH)), 18.2 (CH₂CH₃), 12.9 (CH₂CH₃); Elem. anal. calcd. for C₁₆H₂₈N₃O₃I (437.32): C 43.94, H 6.45, N 9.61; found: C 44.05, H 6.31, N 9.61.

Synthesis of 5b. To a solution of **3** (100 mg, 0.40 mmol) in MeCN (15 mL) were added NaHCO₃ (133 mg, 1.58 mmol) and MeI (0.1 mL, 1.58 mmol) and the reaction mixture was stirred at reflux for 22 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (SiO₂, CH₂Cl₂/MeOH 4:1) to give the imidazolium salt **5b** as a hygroscopic pale yellow oil (87 mg, 54% yield).

¹H NMR (360 MHz, CDCl₃) δ 9.30 (s, 1H, C_εH), 7.73 (d, ³J_{HH} = 8.0 Hz, 1H, NH), 7.38 (s, 1H, C_δH), 4.66 (ddd, ³J_{HH} = 8.8, 8.0, 4.3 Hz, 1H, C_αH), 4.01-4.08 (m, 2H, COOCH₂), 3.89 (s, 3H, NCH₃), 3.85 (s, 3H, NCH₃), 3.27 (dd, ²J_{HH} = 15.9 Hz, ³J_{HH} = 8.8 Hz, 1H, C_βH₂), 3.14 (dd, ²J_{HH} = 15.9 Hz, ³J_{HH} = 4.3 Hz, 1H, C_βH₂), 1.95 (s, 3H, CH₃CO), 1.53 (quintet, ³J_{HH} = 7.5 Hz, 2H, CH₂CH₂CH₃), 1.25 (sextet, ³J_{HH} = 7.5 Hz, 2H, CH₂CH₃), 0.81 (t, ³J_{HH} = 7.5 Hz, 3H, CH₂CH₃); ¹³C{¹H}NMR (90 MHz, CDCl₃) δ 170.9 (C=O), 170.0 (C=O), 136.4 (C_εH), 131.4 (C_γ), 121.6 (C_δH), 65.7 (COOCH₂), 50.2 (C_αH), 36.6 (NCH₃), 34.2 (NCH₃), 30.0

(CH₂CH₂CH₃), 25.2 (C_βH₂), 22.9 (CH₃CO), 18.7 (CH₂CH₃), 13.4 (CH₂CH₃); Elem. anal. calcd. for C₁₄H₂₄N₃O₃I (409.27) × H₂O: C 39.35, H 6.13, N 9.83; found: C 39.19, H 5.86, N 9.88.

Synthesis of 6a. A mixture of **5a** (500 mg, 1.14 mmol) and Ag₂O (265 mg, 1.14 mmol) in dry CH₂Cl₂ (25 mL) was stirred at reflux for 15 h in the dark. After filtration of the cold mixture through Celite, solid [Ru(cym)Cl₂]₂ (350 mg, 0.57 mmol) was added to the filtrate and stirring in the absence of light was continued for 2.5 h. The reaction mixture was subsequently filtered through Celite and the volatiles were removed under reduced pressure. The residue was purified by flash chromatography (SiO₂, MeCN/H₂O 9:1), thus affording pure **6a** as a brown-orange solid (353 mg, 50% yield).

¹H NMR (500 MHz, CDCl₃, 50 °C) δ 6.92 (br, 1H, C_δH), 5.39-5.49 (m, 2H, C_{cym}H), 5.22 (septet, ³J_{HH} = 6.7 Hz, 1H, NCHMe₂), 5.09 (d, ³J_{HH} = 5.7 Hz, 2H, C_{cym}H), 4.78 (br, 1H, C_αH), 4.09-4.18 (m, 2H, COOCH₂), 3.87 (br, 3H, NCH₃), 3.07-3.10 (m, 1H, C_βH₂), 2.96 (septet, ³J_{HH} = 7.0 Hz, 1H, C_{cym}CHMe₂), 2.79 (br, 1H, C_βH₂), 2.05 (s, 3H, C_{cym}CH₃), 1.96 (br, 3H, CH₃CO), 1.60-1.64 (m, 2H, CH₂CH₂CH₃), 1.35-1.40 (m, 2H, CH₂CH₃), 1.37 (d, ³J_{HH} = 6.7 Hz, 6H, NCH(CH₃)₂), 1.29 (d, ³J_{HH} = 7.0 Hz, 6H, C_{cym}CH(CH₃)₂), 0.93 (t, ³J_{HH} = 7.3 Hz, 3H, CH₂CH₃), NH not resolved; ¹³C{¹H}NMR (125 MHz, CDCl₃, 50 °C) δ 173.6 (C_{carbene}), 171.1 (C=O), 170.3 (C=O), 131.5 (C_γ), 117.4 (C_δH), 108.8 (C_{cym}), 98.4 (C_{cym}), 86.5 (C_{cym}H), 85.3 (C_{cym}H), 82.4 (br, 2 × C_{cym}H), 65.9 (COOCH₂), 52.4 (NCHMe₂), 50.6 (C_αH), 36.8 (NCH₃), 31.0 (C_{cym}CHMe₂), 30.7 (CH₂CH₂CH₃), 28.3 (C_βH₂), 24.9 (2 × NCH(CH₃)₂), 23.4 (C_{cym}CH(CH₃)₂), 23.1 (CH₃CO), 21.9 (C_{cym}CH(CH₃)₂), 19.2 (CH₂CH₃), 18.9 (C_{cym}CH₃), 13.7 (CH₂CH₃); Elem. anal. calcd. for C₂₆H₄₁N₃O₃Cl₂Ru (615.60) : C 50.73, H 6.71, N 6.83; found: C 50.50, H 6.50, N 6.77.

Synthesis of 6b. Complex **6b** was synthesised according to the procedure described for **6a**, starting from **5b** (200 mg, 0.49 mmol) and Ag₂O (113 mg, 0.49 mmol) in dry CH₂Cl₂ (10 mL) and subsequent addition of [Ru(cym)Cl₂]₂ (150 mg, 0.24 mmol). After flash chromatography (SiO₂, MeCN/H₂O 90:10), complex **6b** was isolated as a brown-orange solid (152 mg, 53 % yield).

¹H NMR (500 MHz, toluene-*d*₈) δ 7.81 (d, 1H, NH), 6.89 (br, 1H, C_δH), 5.20 (d, ³J_{HH} = 5.4 Hz, 1H, C_{cym}H), 5.11-5.15 (m, 1H, C_αH), 4.84 (br, 2H, C_{cym}H), 4.55 (d, ³J_{HH} = 5.7 Hz, 1H, C_{cym}H), 4.07-4.18 (m, 2H, COOCH₂), 3.88 (s, 3H, NCH₃), 3.73 (s, 3H, NCH₃), 3.01-3.04 (m, 1H, C_βH₂), 2.91 (septet, ³J_{HH} = 6.8 Hz, CH(CH₃)₂), 2.70 (br, 1H, C_βH₂), 2.07 (s, 3H, CH₃CO), 1.69 (s, 3H, C_{cym}CH₃), 1.49-1.58 (m, 2H, CH₂CH₂CH₃), 1.28-1.36 (m, 2H, CH₂CH₃), 1.22 (d, ³J_{HH} = 6.7 Hz, 3H, CH(CH₃)₂), 1.12 (d, ³J_{HH} = 6.8, 3H, CH(CH₃)₂), 0.87 (t, ³J_{HH} = 7.4 Hz, 3H, CH₂CH₃); ¹³C{¹H}NMR (125 MHz, toluene-*d*₈) δ 172.9 (C_{carbene}), 171.5 (C=O), 170.4 (C=O), 131.2 (C_γ), 125.6 (C_δH), 110.9 (C_{cym}), 97.6 (C_{cym}), 87.7 (C_{cym}H), 84.4 (C_{cym}H), 82.1 (C_{cym}H), 81.6 (C_{cym}H), 65.3 (COOCH₂), 50.1 (C_αH), 39.0 (NCH₃), 35.7 (NCH₃), 31.1 (CH₂CH₂CH₃), 31.0 (CH(CH₃)₂), 26.9 (C_βH₂), 23.5 (CH₃CO), 23.2 (CH(CH₃)₂), 21.4 (CH(CH₃)₂), 19.6 (CH₂CH₃), 18.3 (C_{cym}CH₃), 14.0 (CH₂CH₃); Elem. anal. calcd. for C₂₄H₃₇N₃O₃Cl₂Ru (587.54): C 49.06, H 6.35, N 7.15; found: C 48.88, H 6.20, N 6.86.

General procedure for the transfer hydrogenation. The catalyst (0.01 mmol) and *i*-propanol (5 mL) were placed in a one-neck round-bottom flask equipped with a stirring bar and a reflux condenser. The mixture was heated at reflux until complete dissolution. A solution of KOH (2 M, 0.05 mL, 0.1 mmol) was added and the solution was stirred at reflux for 10 min. Benzophenone (182.2 mg, 1.00 mmol) was added and heating was continued. Aliquots (0.2 mL) were taken after 30 min and 2 h, poured into cyclohexane (2 mL), filtered through silica gel in a pasteur pipette and washed with Et₂O (3 × 2 mL). All volatiles were

removed under reduced pressure and the residue dried under high vacuum. Conversions were determined by ^1H NMR spectroscopy using CDCl_3 or DMSO-d_6 as solvent.

X-ray crystallography. Crystals of **6a** were obtained as yellow needles. The intensity data for a crystal of size $0.35 \times 0.10 \times 0.05\text{mm}^3$ were collected at 173K on a Stoe Mark II-Image Plate Diffraction System^{S4} equipped with a two-circle goniometer and using MoK α graphite monochromated radiation (image plate distance 135 mm). The structure was solved by Direct methods using the programme SHELXS-97.^{S5} The refinement and all further calculations were carried out using SHELXL-97.^{S5} The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2 . A multi-scan absorption correction was applied using the MULscanABS routine in PLATON.^{S6}

The alkyl chains are thermally disordered. In the final cycles of refinement their anisotropic displacement parameters were made equal to one another, using the EADP instruction in SHELXL, and the C-C bonds were refined with distance restraints of 1.54(2) Å. CCDC 804412 contains 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.

Table S1 - Crystal Data and Details of the Structure Determination

Formula	C ₂₆ H ₄₁ C ₁₂ N ₃ O ₃ Ru
Formula Weight	615.59
Crystal System	Monoclinic
Space group	P2 ₁ /c (No. 14)
a, b, c [Å]	11.1246(13) 10.9646(9) 24.403(3)
α, β, γ [deg]	90 92.472(10) 90
V [Å ³]	2973.8(6)
Z	4
D(calc) [g cm ⁻³]	1.375
Mu(MoKa) [mm ⁻¹]	0.737
F(000)	1280
Crystal Size [mm]	0.05 × 0.10 × 0.35
Temperature (K)	173
Radiation [Å]	MoKα, 0.71073
θ min, max [deg]	1.7, 25.1
Tot., Uniq. Data, R(int)	19658, 5293, 0.206
Observed data [I > 2.0 σ(I)]	1941
N(ref), N(par)	5293, 244
R, wR ₂ , S	0.0679, 0.1717, 0.76
$w = 1/[\Sigma(F_o^2) + (0.0627P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	
Min. and Max. Resd. Dens. [e Å ⁻³]	-0.84, 0.60

Table S2. Bond Distances (Å)

Ru1–C11 2.407(3)	C2–C3 1.346(15)
Ru1–C12 2.430(3)	C2–C7 1.478(14)
Ru1–C1 2.067(10)	C4–C6 1.542(15)
Ru1–C17 2.175(13)	C4–C5 1.514(14)
Ru1–C18 2.181(12)	C7–C8 1.495(15)
Ru1–C19 2.219(13)	C8–C11 1.471(15)
Ru1–C20 2.207(12)	C9–C10 1.464(16)
Ru1–C21 2.242(14)	C12–C13 1.517(19)
Ru1–C22 2.202(14)	C13–C14 1.52(2)
O1–C9 1.252(13)	C14–C15 1.492(19)
O2–C11 1.344(15)	C17–C22 1.37(2)
O2–C12 1.433(16)	C17–C18 1.42(2)
O3–C11 1.194(15)	C18–C19 1.420(18)
N1–C1 1.347(12)	C19–C26 1.535(19)
N1–C2 1.424(12)	C19–C20 1.442(19)
N1–C16 1.463(13)	C20–C21 1.37(2)
N2–C1 1.367(12)	C21–C22 1.462(18)
N2–C3 1.382(13)	C22–C23 1.522(19)
N2–C4 1.450(13)	C23–C24 1.521(18)
N3–C8 1.470(13)	C23–C25 1.504(18)
N3–C9 1.346(14)	N3–H3A 0.8800

Table S3. Bond Angles (deg)

Cl1–Ru1–Cl2	84.00(10)	O1–C9–C10	124.8(11)	C11–O2–C12	115.8(9)
Cl1–Ru1–C1	88.4(3)	O1–C9–N3	118.8(10)	C1–N1–C2	113.0(8)
Cl1–Ru1–C17	120.1(4)	N3–C9–C10	116.5(10)	C1–N1–C16	127.2(8)
Cl1–Ru1–C18	157.9(4)	O2–C11–C8	113.5(10)	C2–N1–C16	119.5(8)
Cl1–Ru1–C19	154.2(3)	O2–C11–O3	124.2(10)	C1–N2–C3	110.7(8)
Cl1–Ru1–C20	116.6(4)	O3–C11–C8	122.1(11)	C1–N2–C4	127.5(8)
Cl1–Ru1–C21	91.3(4)	O2–C12–C13	105.9(11)	C3–N2–C4	121.5(8)
Cl1–Ru1–C22	93.5(4)	C12–C13–C14	110.7(12)	C8–N3–C9	123.5(8)
Cl2–Ru1–C1	89.1(3)	C13–C14–C15	111.2(12)	Ru1–C1–N1	127.6(7)
Cl2–Ru1–C17	155.9(4)	Ru1–C17–C22	72.8(8)	Ru1–C1–N2	128.8(6)
Cl2–Ru1–C18	118.0(4)	Ru1–C17–C18	71.3(7)	N1–C1–N2	103.6(8)
Cl2–Ru1–C19	91.1(4)	C18–C17–C22	123.1(12)	N1–C2–C3	103.2(8)
Cl2–Ru1–C20	91.2(3)	Ru1–C18–C19	72.6(7)	C3–C2–C7	129.9(9)
Cl2–Ru1–C21	114.9(3)	Ru1–C18–C17	70.8(8)	N1–C2–C7	126.8(9)
Cl2–Ru1–C22	153.3(3)	C17–C18–C19	117.9(12)	N2–C3–C2	109.4(9)
C1–Ru1–C17	91.7(4)	Ru1–C19–C20	70.6(7)	N2–C4–C6	109.7(8)
C1–Ru1–C18	89.9(4)	Ru1–C19–C26	127.4(9)	N2–C4–C5	113.2(8)
C1–Ru1–C19	116.9(4)	C18–C19–C26	119.0(12)	C5–C4–C6	110.7(8)
C1–Ru1–C20	154.9(4)	C20–C19–C26	122.8(11)	Ru1–C21–C22	69.3(7)
C1–Ru1–C21	155.8(4)	C18–C19–C20	118.0(13)	Ru1–C21–C20	70.6(8)
C1–Ru1–C22	117.5(4)	Ru1–C19–C18	69.7(7)	C20–C21–C22	116.2(12)
C17–Ru1–C18	38.0(6)	C19–C20–C21	124.3(12)	Ru1–C22–C21	72.3(8)
C17–Ru1–C19	67.2(5)	Ru1–C20–C21	73.4(7)	Ru1–C22–C17	70.7(8)
C17–Ru1–C20	78.1(5)	Ru1–C20–C19	71.4(7)	C17–C22–C23	117.5(11)
C17–Ru1–C21	67.6(5)	C18–Ru1–C21	81.4(5)	C21–C22–C23	122.0(12)
C17–Ru1–C22	36.5(5)	C18–Ru1–C22	68.0(5)	Ru1–C22–C23	132.6(9)
C18–Ru1–C19	37.6(5)	C19–Ru1–C20	38.0(5)	C17–C22–C21	120.4(13)
C18–Ru1–C20	68.0(5)	C19–Ru1–C21	67.8(5)	C24–C23–C25	107.8(10)
C2–C7–C8	114.3(9)	C19–Ru1–C22	79.7(5)	C22–C23–C24	112.2(10)
N3–C8–C7	111.6(8)	C20–Ru1–C21	36.0(5)	C22–C23–C25	107.8(11)
C7–C8–C11	114.4(9)	C20–Ru1–C22	66.2(5)		
N3–C8–C11	113.6(8)	C21–Ru1–C22	38.4(5)		

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