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Synthesis of a Dinuclear Platinum−Silver Complex Containing a Reactive Acetone Imine Prepared in Situ from Acetone and Ammonia and Stabilized by Metal Complexation

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Summary: The highly reactive acetone imine can be synthesized, from acetone and ammonia, and stabilized in situ by coordination to a silver atom in a very selective process which involves the presence of an (azaindolato)(pentafluorophenyl)platinum(II) complex. The stability of the dinuclear complex allows full characterization of the acetone imine molecule and provides a route to stabilize new, reactive imines.

Introduction

It is well-known that the platinum center in anionic[1,2] or neutral platinum[3,4] complexes behaves as a Lewis base and that this makes them very useful precursors for the synthesis of heteropolynuclear complexes containing donor−acceptor Pt−M bonds (M = Ag, Sn, Pb, Hg, Cd).[5−11] (Perhalophenyl)platinate derivatives form, through adequate reactions, a family of complexes containing a Pt_xAg skeleton.[2]

One of the greatest difficulties found in the preparation of (pentafluorophenyl)platinate complexes containing Pt−Ag bonds is, however, the recurrence of arylating processes. These result in the formation of AgC_6F_5, thus preceding the formation of the corresponding complexes with Pt→Ag bonds. The higher the number of C_6F_5 groups bonded to platinum, the higher the transmetalating capability of the platinate fragment.[12,13] Given this, we considered that one of the ways to maintain the anionic character of the platinum substrates (i.e. a higher basic character) would be by substituting one or two C_6F_5 groups by other anionic ligands. We have thus reported that $[NBu_4][Pt(C_6F_5)_2acac]$ reacts with $AgClO_4$ in a 2:1 or 1:1 molar ratio, yielding tri- or tetranuclear complexes, respectively, in which the Pt−Ag bonds are unsupported by any covalent bridging ligand.[12,14]

With this in mind, we decided to prepare the dianionic complex $[NBu_4]_2[Pt(C_6F_5)_3(\text{azaindolate})]$ (**A**) in order to test its usefulness in the formation of these types of polynuclear complexes, since the azaindolate ligand is anionic and a well-known bridging ligand[15−17] which could, in addition, support the Pt−M bond if formed.

However, attempts to prepare complex **A** by reacting $[NBu_4][Pt(C_6F_5)_3(\text{thf})]$ with tetrabutylammonium azaindolate resulted in the formation of a mixture of the two isomers (the one containing the anionic aza ligand bonded to the platinum center through the N atom of the pyridine ring and the other with the anionic aza ligand coordinated by the N atom of the pyrrole ring).[18] To avoid this mixture, we were obliged to use a different synthetic approach (formation of $[Pt(C_6F_5)_3(\text{azaindole})]^-$ and once formed test the deprotonation of the azaindole ligand), which resulted in the formation of a binuclear Pt/Ag complex, both metals being supported by the azaindolate ligand but the silver containing as well the unusual acetone imine ligand. The formation of this complex is the subject of the present paper.

Results and Discussion

$[NBu_4][Pt(C_6F_5)_3(HN_2C_7H_5)]$ (**1**), containing a 7-azaindole ligand, has been prepared by treating $[NBu_4]_2[Pt(C_6F_5)_3Cl]$ with $AgClO_4$ in THF (tetrahydrofuran) and addition of the azaindole (1:1 molar ratio). The ^{1}H NMR spectrum of complex **1** in $CDCl_3$ at room temperature shows a downfield-shifted signal (10.11 ppm), which corresponds to the hydrogen bonded to the nitrogen atom, but without platinum satellites. The other five hydrogen atoms of the Haza ligand appear as individual signals in the range between 6.4 and 8.5 ppm. The hydrogen atom at the ortho position of the pyridine ring (8.46 ppm) shows platinum satellites ($J_{Pt-H} = 28$ Hz),

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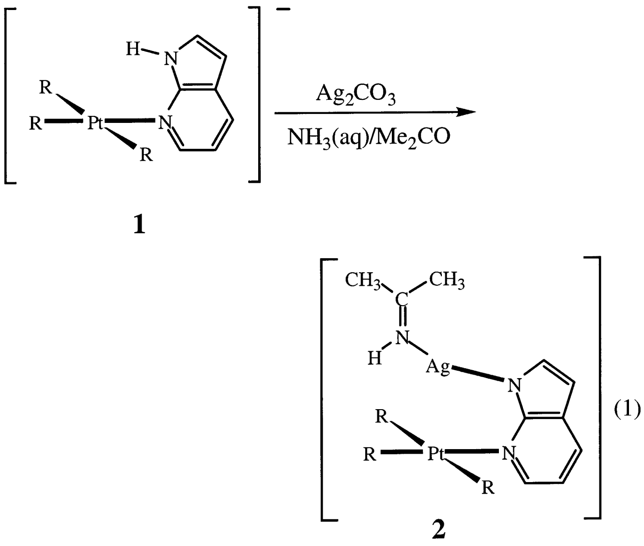
thus indicating that the Haza ligand is coordinated to the platinum atom through the pyridine ring. The ^{19}F NMR spectrum in $CDCl_3$ at room temperature shows that there are two types of C_6F_5 groups, the halves of each group being equivalent (see Experimental Section). The low-temperature ^{1}H NMR spectrum of complex **1** in CD_2Cl_2 does not reveal any important differences from the room-temperature NMR spectrum. Due to the low temperature none of the signals show platinum satellites. However, the ^{19}F NMR spectra in CD_2Cl_2 at low temperature show four signals for the ortho fluorine atoms (2:1:1:2 ratio), indicating a static situation on the NMR time scale.

In a attempt to produce the deprotonation of the azaindole and to simultaneously prepare a polynuclear compound, we performed the reaction of **1** in acetone with Ag_2CO_3. This reagent contains the deprotonating agent CO_3^{2-} and simultaneously liberates silver cations, which are well-recognized Lewis acids. Under these conditions no reaction took place, probably due to the insolubility of the Ag_2CO_3 in acetone. However, when a small amount of NH_3(aq) solution was added dropwise, a reaction took place instantaneously, giving rise to an unexpected result. From the solution the heterodinuclear complex $[NBu_4][(C_6F_5)_3Pt(\mu\text{-aza})Ag(HN{=}CMe_2)]$ (**2**) was obtained. This compound, the structure of which has been established by X-ray diffraction, contains a molecule of acetone imine stabilized by coordination to the silver center, as will be discussed later (eq 1).



1

2

(1)

Complex **2** is stable at room temperature in the solid state and in the absence of light. Under similar conditions, its acetone solution does not decompose for at least 5 days.

The participation of NH_3 in the reaction is crucial, since the unreacted materials are obtained if ammonia is not present in the solution. No evidence of the intermediates which finally result in the formation of **2** can be obtained from the reaction mixture.

The IR spectrum of **2** shows some characteristic absorptions of the acetone imine ligand at 3334 and 1667 cm^{-1} which are due to ν(N−H) and ν(C=N), respectively. These absorptions appear at frequencies similar to those described for the acetone imine tungsten ($[W(PhC{\equiv}CPh)_3(NH{=}CMe_2)]$),[19] ruthenium ($[Ru(bpy)_2(NH{=}CMe_2)_2][PF_6]_2$),[20] and gold ($[Au(NH{=}CMe_2)_2]CF_3SO_3$)[21] complexes and are also similar to the values found for the dimerized acetone imine by intramolecular hydrogen bridges (ν(C=N), 1658, 1670 (sh) cm^{-1}; ν(N−H), 3293 cm^{-1}).[22]

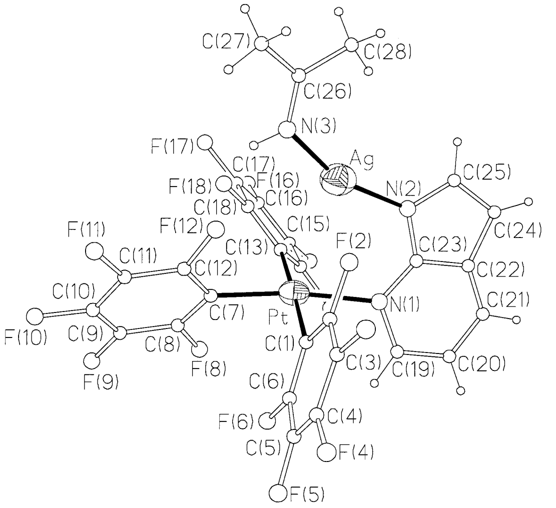


Figure 1. Perspective drawing of the $[(C_6F_5)_3Pt(\mu\text{-aza})Ag(HN{=}CMe_2)]^-$ anion.

The ^{1}H NMR spectrum of **2** in $CDCl_3$ at room temperature shows, in addition to the signals due to the NBu_4^+ cation, five signals which can be assigned to the 7-azaindolate (aza$^-$) and three signals which can be assigned to the acetone imine ligand (δ 2.20 (s, 3H, $-CH_3$), 2.32 (s, 3H, $-CH_3$), 8.98 (sharp s, 1H, $-NH$)). These latter signals compare well with those described for the tungsten (δ 1.23 (s, 3H, $-CH_3$), 2.23 (s, 3H, $-CH_3$), 11.47 (broad s, 1H, $-NH$)) and gold (δ 2.39 (d, 3H, $-CH_3$), 2.46 (s, 3H, $-CH_3$), 10.28 (broad-s, 1H, $-NH$)) complexes. The signal due to the hydrogen bonded to the nitrogen atom appears in **2** at a lower chemical shift than in the other cases.

Crystal Structure of $[NBu_4][(C_6F_5)_3Pt(\mu\text{-aza})Ag(HN{=}CMe_2)]$. Figure 1 shows the structure of the anion. Relevant bond distances and angles are shown in Table 2. The platinum atom is in a square-planar environment formed by the three pentafluorophenyl groups and the azaindolato ligand. This acts as a bridge between the platinum and silver centers. In addition, there is an imino group bonded to the silver atom. The Pt−C and Pt−N distances and angles around the metal atom (see Table 2) are within the range usually found for this kind of Pt(II) complex.[23−25] The dihedral angle between the platinum coordination plane and the azaindolato plane is 65.7(3)°. The angles between the C_6F_5 rings and the platinum coordination plane are 75.2(4)° for the C1 group, 68.2(4)° for the C7 group, and 57.2-

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Table 1. Crystal Data and Structure Refinement Details for $[NBu_4][(C_6F_5)_3Pt(\mu\text{-aza})Ag(HN{=}CMe_2)]$ (2)

empirical formula	$C_{44}H_{48}AgF_{15}N_4Pt$
unit cell dimens	
a (Å)	11.939(4)
b (Å)	14.143(4)
c (Å)	15.686(5)
α (deg)	65.66(2)
β (deg)	87.270(14)
γ (deg)	74.612(12)
V (Å^3), Z	2321.1(13), 2
wavelength (Å)	0.710 73
temp (K)	200(1)
radiation	graphite-monochromated Mo Kα
cryst syst	triclinic
space group	$P\bar{1}$
cryst dimens (mm)	0.27 × 0.15 × 0.11
abs coeff (mm^{-1})	3.528
transmissnfactors	1.000, 0.567
abs cor	ψ scans
diffractometer	Siemens STOE/AED2
2θ range for data collen (deg)	4.1−47.0 ($\pm h$, $\pm k$, $+l$)
no. of rflns collected	7144
no. of indep rflns	6853 (R(int) = 0.0595)
refinement method	full-matrix least squares on F^2
goodness of fit on F^2	1.086
final R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0693 wR2 = 0.1647
R indices (all data)[a]	R1 = 0.0983 wR2 = 0.1882

[a] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{0.5}$; $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[NBu_4][(C_6F_5)_3Pt(\mu\text{-aza})Ag(HN{=}CMe_2)]$ (2)

Pt−C(1)	2.052(14)	Pt−C(7)	2.007(12)
Pt−C(13)	2.079(14)	Pt−N(1)	2.116(11)
Ag−N(2)	2.092(15)	Ag−N(3)	2.096(16)
N(3)−C(26)	1.303(23)		
C(7)−Pt−C(13)	90.2(5)	C(7)−Pt−N(1)	172.0(5)
C(13)−Pt−N(1)	93.2(5)	C(7)−Pt−C(1)	88.4(5)
C(13)−Pt−C(1)	177.4(6)	N(1)−Pt−C(1)	87.8(5)

(5)° for the C13 group. The short N3−C26 distance, 1.303(23) Å, is in keeping with the multiplicity of this C═N bond.[26] Moreover, the angles around N3 (Ag−N3−C26 = 125.3(16)°) and C26 atoms (N3−C26−C27 = 120.3(23)°, N3−C26−C28 = 119.9(21)°, C27−C26−C28 = 119.7(21)°) are those expected for sp^2-hybridized atoms. The C26−C27 and C26−C28 distances (1.443(29) and 1.537(31) Å, respectively) are those expected for C−C single bonds. The C−N distance is the usual one for a C═N double bond and is very similar to those observed in the tungsten (1.284(7) Å)[19] and gold derivatives (1.271(7) and 1.285(8) Å)[21,27] but longer than the distance found in the ruthenium complex (1.16(2) Å).[20] The range of angles around these carbon atoms is characteristic of sp^2 hybridization and quite similar to that observed in the tungsten (116.6(5)−122.6(5)°) and gold complexes (116.9(6)−120.4(7)°), in sharp contrast to the range of values obtained for the ruthenium complex (99−148°). Some differences are also observed between the three complexes in the M−N═C angles, these being 159(1), 136.2(4), and 125.3(16)° for ruthenium, tungsten, and platinum complexes, respectively, possibly forced by the metal environment.

In addition, H3 forms a N3−H3···F12 hydrogen bridging bond, the H3−F12 distance being 2.117 Å. The position of the H3 atom was geometrically generated on the basis of its N3 parent atom, with a N3−H3 distance fixed at 0.900 Å.

As far as the Ag environment is concerned, it can be said that the silver center is two-coordinate, the Ag−N distances being equal within experimental error and similar to (imidazole and succinimide N-donor ligands)[28−30] or shorter than (pyridine and amine ligands)[31] those found in other complexes containing Ag−N bonds. The N2−Ag−N3 angle is, however, only 160.1(6)°. Whether this perceptibly bent angle is due to a weak Ag···Pt interaction (3.004(2) Å)[32] or to the geometrical constraints imposed by the bulkiness of the ligands in the molecules, the existence of an intramolecular N−H···F bridging bond, or both remains unclear.

The reaction described to give complex **2** is noteworthy, since direct synthesis of −NH ketone imines from ketones and ammonia requires drastic conditions and the acetone imine is a very short-lived molecule that polymerizes even in dilute solutions at temperature around 200 K. N-Unsubstituted imines are very reactive substances under normal conditions (300 K, 1 bar, air) and suffer immediate polymerization, oxidation, or hydrolysis.[33−36] Aliphatic imines of low molecular weight containing a N−H bond polymerize spontaneously at temperatures below 273 K; however, imines with bulky or electronegative substituents are much more stable. Some examples of the formation and stabilization of imines through deprotonated amido species of Co(III), Ru(III), and Pt(IV) have been described by Sargeson et al.,[37−39] although in most of them the imine ligand contains large substituents and the chelate effect aids its stabilization. The formation and incorporation of the acetone imine molecule acting as a ligand has been reported recently.[19−21] In two of the cases[19,20] a C−N bond was already present in the organic precursor ligand: Yeh et al. have prepared the complex $[W(PhC{\equiv}CPh)_3(NH{=}CMe_2)]$ by reduction with MeLi of the acetonitrile coordinated to tungsten and subsequent hydrolysis,[19] while Wong et al obtained $[Ru(bpy)_2(NH{=}CMe_2)_2][PF_6]_2$ by the electrochemical oxidation of 2,3-dimethyl-2,3-diaminobutane coordinated to ruthenium in a pH-dependent route.[20] Very recently the acetone imine gold complex $[Au(NH{=}CMe_2)_2]CF_3SO_3$ has been

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prepared by reaction of NH_3 with ketones[21] in a pathway which also requires C═N bond formation. Some other acetone imine gold complexes have been obtained from this compound.[27,40]

The stabilization reaction of the acetone imine described in this paper is highly selective. The Ag_2CO_3 and $[NBu_4][Pt(C_6F_5)_3(Haza)]$ salts are both necessary. Ag_2CO_3 does not react appreciably with the acetone/ammonia solution under the described conditions in the absence of the platinum complexes (see Experimental Section), and the platinum complexes remain unreacted and can be recovered from the acetone/ammonia solution if the silver salt is not present.

To check the generality of the formation and stabilization of the acetone imine, we have also carried out reactions between complex **1** and $NiCO_3$ or $CuCO_3$ under similar conditions (acetone/ammonia solution) without success.

Experimental Section

General Methods. C, H, and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. The IR spectra were recorded over the range 4000−200 cm^{-1} on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. The ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Varian XL-200 or a Unity-300 instrument in $CDCl_3$ or acetone-d_6 solutions. All reactions in which silver salts are involved were carried out with exclusion of light. 7-Azaindole was used as received from Aldrich. $[NBu_4]_2[Pt(C_6F_5)_3Cl]$[41] and Ag_2CO_3[42] were prepared as described elsewhere.

Safety Note. Perchlorate salts are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Synthesis of $[NBu_4][Pt(C_6F_5)_3(HN_2C_7H_5)]$ (1). To a solution of 1.000 g (0.822 mmol) of $[NBu_4]_2[Pt(C_6F_5)_3Cl]$ in 25 mL of thf was added 0.170 g (0.822 mmol) of $AgClO_4$. The solution, protected from the light, was stirred at room temperature for 30 min. The AgCl was separated by filtration, and the solution was evaporated to dryness. The residue was dissolved in 30 mL of CH_2Cl_2, and 0.097 g (0.822 mmol) of 7-azaindole was added to the resulting solution. After 1 h of stirring the solution was evaporated to dryness and the residue was treated with 20 mL of ^{i}PrOH, yielding a white solid (**1**) which was filtered off and washed with *n*-hexane. Yield: 76%. Anal. Found (calcd): C, 46.52 (46.59); H, 4.18 (4.00); N, 4.31 (3.97). IR (Nujol; cm^{-1}): C_6F_5, X-sensitive mode,[43] 800 m, 788 m, 773 m; other, 1633 m, 1607 m, 1496 vs, 1055 s, 954 s; Haza (N−H), 3433 m; other, 1667 m, 804 m, 522 m, 476 m, 447 w; NBu_4, 883 m. ^1H NMR ($CDCl_3$, room temperature): δ Haza, 10.11 (s,1H), 8.46 (d, 1H, $J_{Pt-H} = 28$ Hz), 7.78 (d, 1H), 7.33 (t, 1H), 6.86 (dd, 1H), 6.43 (t, 1H); NBu_4, 0.95 (t, 12H, $-CH_3$), 1.38 (sext, 8H, α-CH_2), 1.61 (m, 8H, β-CH_2), 3.12 (m, 8H, γ-CH_2). ^{19}F NMR ($CDCl_3$, room temperature): δ *o*-F, −116.95 (d, 2F, $J_{Pt-o-F} = 527$ Hz), −117.85 (d, 4F, $J_{Pt-o-F} = 357$ Hz); *m*-F, −164.83 (m, 4F), −165.03 (m, 2F); *p*-F, −164.98 (t, 1F), −166.79 (t, 2F). ^1H NMR (CD_2Cl_2, −90 °C): δ Haza, 9.94 (d, 1H), 8.42 (d 1H), 7.86 (t, 1H), 7.36 (d, 1H), 6.92 (m, 1H), 6.48 (d, 1H). ^{19}F NMR (CD_2Cl_2, −90 °C): δ *o*-F, −117.40 (2F), −117.98 (1F), −118.62 (1F), −119.65 (2F); *m*-F and *p*-F, −164.67 (6F), −166.58 (3F).

Synthesis of $[NBu_4][(C_6F_5)_3Pt(\mu\text{-aza})Ag(HN{=}CMe_2)]$ (2). To a solution of 0.200 g (0.189 mmol) of **1** in 30 mL of acetone was added 0.052 g (0.095 mmol) of Ag_2CO_3 (2:1 molar ratio), and then 1 mL of a aqueous solution of ammonia (7.6 M) was added dropwise to this suspension, producing immediate dissolution of the Ag_2CO_3. After 2 h of stirring in the absence of light the colorless solution was evaporated to dryness. The addition of 20 mL of *n*-hexane rendered a white solid (**2**), which was filtered off. Yield: 73%. Anal. Found (calcd): C, 42.93 (43.29); H, 4.06 (3.96); N, 4.46 (4.58). IR (Nujol; cm^{-1}): C_6F_5, X-sensitive mode,[43] 805 m, 785 w, 766 m; others, 1605 m, 1496 vs, 1053 s, 951 s; aza: 1594 m, 793 m; $HN{=}C(CH_3)_2$, ν(C═N) 1667 m, ν(N−H) 3334 m; other 476 m; NBu_4, 883 m. ^1H NMR ($CDCl_3$, room temperature): δ aza, 8.51 (d, 1H), 7.69 (d, 1H), 7.33 (m, 1H), 6.54 (dd, 1H), 6.32 (m, 1H); $HN{=}C(CH_3)_2$: 8.98 (s, 1H, NH), 2.20 (s, 3H, CH_3), 2.32 (s, 3H, CH_3); NBu_4, 0.89 (t, 12H, $-CH_3$), 1.26 (sext., 8H, α-CH_2), 1.44 (m, 8H, β-CH_2), 2.87 (m, 8H, γ-CH_2). ^{19}F NMR ($CDCl_3$, room temperature): δ −116.88 (m, *o*-F, 4F), −117.44 (m, *o*-F, 2F); −166.3 (m, *m*-F + *p*-F, 6F); −167.6 (t, *p*-F, 1F); −168.1 (m, *m*-F, 2F).

Reaction between Ag_2CO_3 and Aqueous Ammonia in Acetone. To a suspension of 0.150 g (0.270 mmol) of Ag_2CO_3 in 30 mL of acetone was added 1 mL of aqueous solution of ammonia (7.6 M) dropwise. After 2 h of stirring in the absence of light the remaining suspension was filtered off and 0.132 g of unreacted Ag_2CO_3 was recovered (88% of the starting material).

Crystal Structure Analysis for $[NBu_4][(C_6F_5)_3Pt(\mu\text{-aza})Ag(HN{=}CMe_2)]$ (2). Crystal data and other details of the structure analysis are presented in Table 1. Suitable crystals of **2** were obtained by slow diffusion of *n*-pentane into a solution of complex **2** in CH_2Cl_2 (3 mL) at −30 °C, and one of them was mounted at the end of a glass fiber. The unit cell dimensions were determined from 60 centered reflections in the range $21.5 < 2\theta < 29.7°$. An absorption correction was applied based on 360 azimuthal scan data. Lorentz and polarization corrections were applied for both structures.

The structure was solved by Patterson and Fourier methods. All refinements were carried out using the SHELXL-93 program.[44] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. For complex **2**, all hydrogen atoms were constrained to idealized geometries and assigned a common isotropic displacement parameter of 0.1058. Full-matrix least-squares refinement of these models against F^2 converged to the final residual indices given in Table 1. Final difference electron density maps showed seven features above 1 e/Å^3 (maximum/minimum +2.86/−1.81 e/Å^3), being closer than 1 Å to the platinum atom.

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Supporting Information Available: Tables of all atomic positional and equivalent isotropic displacement parameters, anisotropic displacement parameters, bond distances and bond angles, hydrogen coordinates, and anisotropic displacement parameters for the crystal structure of complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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