FULL PAPER

DALTON

Synthesis, structure and redox properties of some 2-(arylazo)-phenolate complexes of rhodium(III) †

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Reaction of 2-(arylazo)phenols 2-(4′-RC$_6$H$_4$N=N)C$_6$H$_3$OH(Me-4) (H$_2$ap-R, where H$_2$ stands for the two dissociable protons and R for the substituent in the phenyl ring of the arylazo fragment) with [Rh(PPh$_3$)$_3$Cl] afforded a family of organometallic complexes of rhodium(III) of type [Rh(PPh$_3$)$_2$(ap-R)Cl]. The crystal structure of [Rh(PPh$_3$)$_2$(ap-NO$_2$)Cl] has been determined. The 2-(arylazo)phenols are coordinated *via* dissociation of the phenolic proton and the phenyl proton at the *ortho* position of the phenyl ring in the arylazo fragment, as dianionic tridentate C,N,O-donors forming two five-membered chelate rings. ^{1}H and ^{13}C NMR spectra of the complexes are in excellent agreement with their composition and stereochemistry. The complexes are diamagnetic (low-spin d^6, $S = 0$) and show intense absorptions in the visible and ultraviolet regions. Cyclic voltammetry for all the complexes show a quasi-reversible oxidation within 0.65 to 1.10 V *vs.* SCE and an irreversible reduction within −1.34 to −1.50 V *vs.* SCE. The potential of the oxidation is found to be sensitive to the nature of the substituent R in the 2-(arylazo)phenolate ligand.

Introduction

Transition metal-mediated organic transformations *via* activation of C–H bonds have been an active area of chemical research.[1] Most of these reactions proceed *via* an organometallic intermediate. Hence synthesis of new organometallic complexes is of significant importance, particularly with regard to reaction of the metal–carbon bonds. Herein we report the results of our studies on a group of organorhodium complexes obtained from the reaction of 2-(arylazo)phenols **1** with Wilkinson's catalyst, *viz.* [Rh(PPh$_3$)$_3$Cl]. Rhodium complexes in general and organorhodium complexes in particular are known to exhibit antitumor activities and hence they have wide application as chemotherapeutic agents.[2] Wilkinson's catalyst has been chosen as the rhodium starting material because of its well known efficiency in bringing about catalytic transformations of organic substrates.[3] The reason behind the choice of 2-(arylazo)phenols as the main ligand is manifold. Simple azobenzenes are well known to bind to soft metal centers as monoanionic bidentate C,N-donor ligands forming five-membered metallacycles of type **2**.[4] However, [Rh(PPh$_3$)$_3$Cl] undergoes dissociation in solution producing free PPh$_3$ and a formally three-coordinated Rh^I(PPh$_3$)$_2$Cl fragment. For oxidative addition of organic ligands to this fragment, the incoming organic ligand is desired to be capable of satisfying the residual positive charge of rhodium(III) and the remaining three coordination sites. As phenolate oxygen is a recognized hard donor and a familiar stabilizer of the higher oxidation states of transition metals,[5] we have chosen a modified azobenzene with a potential third donor site, *viz.* the 2-(arylazo)phenols **1**, as our test ligand in this reaction. This strategy
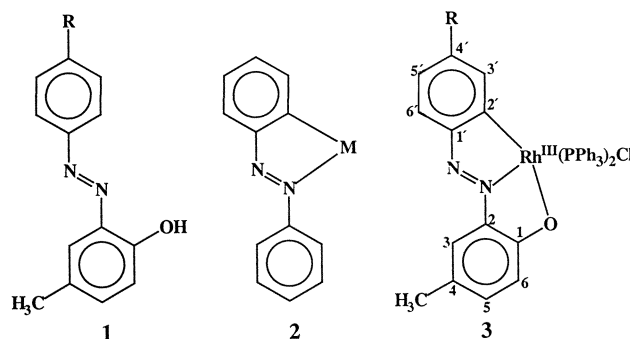
has indeed turned out to be very successful in affording a family of rhodium(III) cyclometallates of type **3**. While there are numerous examples of organorhodium complexes in the literature,[6] cyclometallates of rhodium(III) appear to be relatively less common.[7] The chemistry of the new family of cyclometallated rhodium(III) complexes is described here with special reference to synthesis, characterization and redox properties.

Experimental

Materials

Rhodium trichloride was obtained from Johnson Matthey and triphenylphosphine was purchased from Loba, India. [Rh(PPh$_3$)$_3$Cl] was synthesized following a reported procedure.[8] The *para*-substituted anilines and *p*-cresol were obtained from S.D., India. The 2-(arylazo)phenol ligands were prepared by coupling diazotized *p*-substituted anilines with *p*-cresol. All other chemicals and solvents were reagent grade commercial materials used as received. Purification of dichloromethane, acetonitrile and preparation of tetrabutylammonium perchlorate for electrochemical work were as reported.[9]

Preparations

[Rh(PPh₃)₂(ap-NO₂)Cl]. H₂ap-NO₂ (29 mg, 0.11 mmol) was dissolved in toluene (40 mL) and to it were added [Rh(PPh₃)₃Cl] (100 mg, 0.11 mmol) and triethylamine (58 mg, 0.24 mmol). The mixture was then refluxed under a dinitrogen atmosphere for 3 h, when a green solution was obtained. Evaporation of this solution afforded a dark solid which was purified by thin layer chromatography on a silica plate with toluene as the eluent. A green band separated and the complex was extracted from it with acetonitrile. The green solid, obtained upon evaporation of the solvent, was recrystallized from dichloromethane–hexane to afford [Rh(PPh₃)₂(ap-NO₂)Cl] as a crystalline green solid. Yield: 55%. Calc.: C, 61.70; H, 3.96; N, 4.50. Found: C, 61.69; H, 3.97; N, 4.53%.

[Rh(PPh₃)₂(ap-Cl)Cl]. This complex was prepared and purified by following the above procedure using H₂ap-Cl instead of H₂ap-NO₂ and the reflux time was extended to 5 h. Yield 50%. Calc.: C, 64.84; H, 4.30; N, 3.09. Found: C, 65.09; H, 4.38; N, 3.11%.

[Rh(PPh₃)₂(ap-H)Cl]. This complex was prepared and purified following the same procedure using H₂ap-H instead of H₂ap-Cl and the reflux time was extended to 8 h. Yield 46%. Calc.: C, 67.32; H, 4.58; N, 3.21. Found: C, 67.35; H, 4.60; N, 3.22%.

[Rh(PPh₃)₂(ap-Me)Cl]. This complex was prepared by following the same procedure using H₂ap-Me instead of H₂ap-H and the reflux time was extended to 10 h. Purification was achieved by thin layer chromatography on a silica plate with toluene–acetonitrile (5 : 1) as the eluent. A greenish blue band separated and the complex extracted from it with acetonitrile. The greenish blue solid, obtained upon evaporation of the solvent, was recrystallized from dichloromethane–hexane to afford [Rh(PPh₃)₂(ap-Me)Cl] as a crystalline greenish blue solid. Yield 34%. Calc.: C, 67.61; H, 4.73; N, 3.15. Found: C, 67.63; H, 4.77; N, 3.16%.

[Rh(PPh₃)₂(ap-OMe)Cl]. This complex was prepared and purified by following the same procedure using H₂ap-OMe instead of H₂ap-Me and the reflux time was extended to 23 h. Yield 33%. Calc.: C, 66.42; H, 4.65; N, 3.09. Found: C, 66.44; H, 4.66; N, 3.10%.

Physical measurements

Microanalyses (C,H,N) were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra were obtained on a Perkin-Elmer 783 spectrometer with samples prepared as KBr pellets, electronic spectra on a Shimadzu UV-1601 spectrophotometer. Magnetic susceptibilities were measured using a PAR 155 vibrating sample magnetometer. ¹³C and ¹H NMR spectra were obtained on a Brucker drx 500 NMR spectrometer using TMS as the internal standard. Electrochemical measurements were made under a dinotrogen atmosphere using a PAR model 273 potentiostat. A platinum-disc working electrode, a platinum wire auxiliary electrode and an aqueous saturated calomel reference electrode (SCE) were used in a three electrode configuration. A RE 0089 X-Y recorder was used to trace the voltammograms. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

Crystallography

Single crystals were grown by slow diffusion of hexane into a dichloromethane solution of the complex [Rh(PPh₃)₂(ap-NO₂)-Cl]. Selected crystal data and data collection parameters are

given in Table 1. Data were collected on a SMART CCD diffractometer using graphite monochromated Mo-Kα radiation by ω scan. X-Ray data reduction, structure solution and refinement were done using the SHELXS-97 and SHELXL-97 programs.[10] The structure was solved by direct methods.

CCDC reference number 186/2240.

See http://www.rsc.org/suppdata/dt/b0/b005902l/ for crystallographic files in .cif format.

Results and discussion

Five 2-(arylazo)phenols **4** have been used in the present study. The ligands are abbreviated in general as H₂ap-R, where H₂ stands for two hydrogens (one phenolic and one phenyl (at 2′ position)) that undergo dissociation upon complexation (see below) and R is the substituent at 4′ position of the phenyl ring in the arylazo fragment. Reaction of these ligands with [Rh(PPh₃)₃Cl] proceeds smoothly in refluxing toluene in the presence of triethylamine to afford a family of organorhodium complexes of type [Rh(PPh₃)₂(ap-R)Cl]. Elemental (C, H, N) analytical data are consistent with these compositions. Hence it appears that rhodium exists in the +3 oxidation state in these complexes and the 2-(arylazo)phenol ligands are coordinated as dianionic tridentate C,N,O-donors. Magnetic susceptibility measurements show that the complexes are diamagnetic, which supports the trivalent state of rhodium (low-spin d⁶, $S = 0$). To find out the actual coordination mode of the 2-(arylazo)phenolate ligands and stereochemistry of the complexes the molecular structure of a representative member of the family, *viz.* [Rh(PPh₃)₂(ap-NO₂)Cl], has been determined by X-ray crystallography.

| R	Ligand
OMe	H₂ap-OMe
Me	H₂ap-Me
H	H₂ap-H
Cl	H₂ap-Cl
NO₂	H₂ap-NO₂
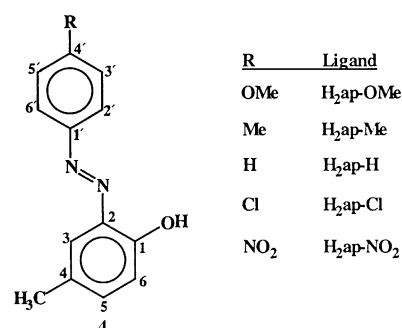
A view of the complex molecule is shown in Fig. 1 and selected bond parameters are listed in Table 2. The 2-(arylazo)phenol ligand is indeed coordinated as a tridentate C,N,O-donor forming two five-membered chelate rings with bite angles of 80.57(9) (O–Rh–N) and 79.69(10)° (N–Rh–C). The 2-(arylazo)phenol ligand, rhodium and chloride constitute the equatorial plane with the latter in *trans* position with respect to the azo-nitrogen, while the two PPh₃ ligands occupy mutually *trans* positions. The CNOP₂Cl coordination sphere around rhodium is distorted octahedral in nature, which is reflected in all the bond parameters around rhodium. Cyclometallates of rhodium(III) of the observed type appear to be unprecedented. The Rh–C, Rh–O, Rh–P and Rh–Cl distances are all quite normal, according to structurally characterized complexes of rhodium(III) containing these bonds.[11] While the Rh–N1 distance is rather short relative to that found in complexes where the Rh–N interaction can only be of σ type,[12] the observed azo N1–N2 distance is longer than when uncoordinated azo.[13] The decrease in Rh–N distance and increase in N–N bond length may be attributed to back bonding from the filled t₂ orbitals of rhodium to the vacant π* orbital localized on the azo function. As all the [Rh(PPh₃)₂(ap-R)Cl] complexes display similar spectral and electrochemical properties (see below), the other four complexes are assumed to have a similar structure to that of [Rh(PPh₃)₂(ap-NO₂)Cl].

**Table 1** Crystallographic data of [Rh(PPh₃)₂(ap-NO₂)Cl]

Empirical formula	$C_{49}H_{39}ClN_3O_3P_2Rh$
M	918.13
Space group	Monoclinic, $P2_1/n$
a/Å	11.9111(2)
b/Å	16.9049(3)
c/Å	21.4067(3)
β/°	96.744(1)
V/Å³	4280.54(12)
Z	4
λ/Å	0.71073
T/°C	22
μ/mm⁻¹	0.582
Reflections collected	29308
Independent reflections	8742 ($R_{int} = 0.0449$)
$R1$	0.0348
$wR2$	0.0823

Table 2 Selected bond parameters (distances in Å, angles in °) for [Rh(PPh₃)₂(ap-NO₂)Cl]

Rh–N(1)	1.951(2)	C(7)–N(2)	1.408(4)
Rh–O(1)	2.181(7)	N(1)–N(2)	1.290(3)
Rh–P(1)	2.3734(7)	N(1)–C(6)	1.386(3)
Rh–P(2)	2.3686(7)	C(6)–C(1)	1.420(4)
Rh–Cl	2.3805(8)	C(1)–O(1)	1.307(4)
Rh–C(12)	1.987(3)		
N(1)–Rh–C(12)	79.69(10)	C(12)–Rh–O(1)	160.25(10)
N(1)–Rh–O(1)	80.57(9)	N(1)–Rh–Cl	178.86(7)
N(1)–Rh–P(2)	91.87(6)	P(1)–Rh–P(2)	176.25(3)
O(1)–Rh–P(2)	92.62(6)	C(7)–C(12)–Rh	110(2)
C(12)–Rh–P(1)	92.52(8)	N(2)–C(7)–C(12)	119.2(2)
C(12)–Rh–P(2)	87.64(8)	N(1)–N(2)–C(7)	109.4(2)
O(1)–Rh–P(1)	88.50(6)	N(2)–N(1)–Rh	121.7(2)
N(1)–Rh–P(1)	91.84(6)	C(6)–N(1)–Rh	116.2(2)
O(1)–Rh–Cl	100.54(6)	N(1)–C(6)–C(1)	113.8(3)
C(12)–Rh–Cl	99.20(8)	O(1)–C(1)–C(6)	122.1(3)
P(2)–Rh–Cl	88.30(3)	C(1)–O(1)–Rh	107.3(2)
P(1)–Rh–Cl	87.98(3)		
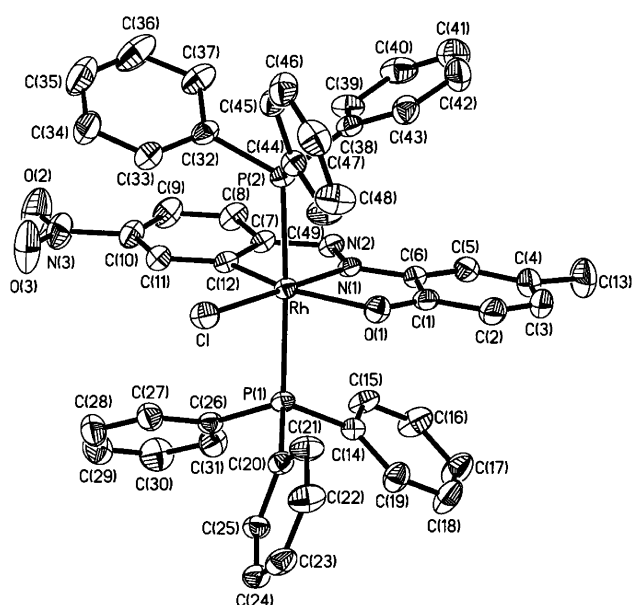
Fig. 1 View of the [Rh(PPh₃)₂(ap-NO₂)Cl] molecule.

¹H NMR spectra of all the complexes have been recorded in CDCl₃ solution. A distinct methyl resonance is displayed by all the five complexes near δ 1.7 which is assigned to the methyl group in the *p*-cresol fragment of the 2-(arylazo)phenolate ligands. Additional methyl signals are observed for [Rh(PPh₃)₂-(ap-Me)Cl] and [Rh(PPh₃)₂(ap-OMe)Cl] at δ 1.86 and 3.45
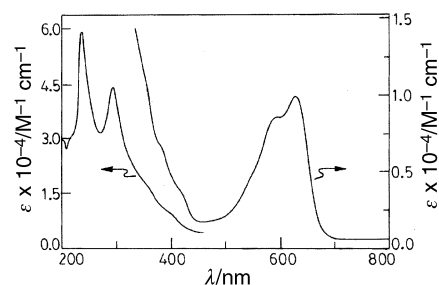
Fig. 2 Electronic spectrum of [Rh(PPh₃)₂(ap-OMe)Cl] in dichloromethane solution.

respectively, which are due to the methyl and methoxy groups in the arylazo fragment of the respective ligand. The aromatic region of the spectra (δ 5.0–8.0) appears a bit complex due to overlap of some signals and hence assignment of all the signals in this region to specific protons has not been possible. However, intensity measurement of the signals corresponds to the total number of aromatic protons present in the respective complexes. ¹³C NMR spectra of the [Rh(PPh₃)₂(ap-R)Cl] complexes were also recorded in CDCl₃ solution. Each complex displays the expected number of signals. The PPh₃ ligands show four intense signals near δ 128, 129, 130 and 135 in an intensity ratio of 1:2:1:2. The methyl carbon in the *p*-cresol fragment of the 2-(arylazo)phenolate ligands shows an isolated signal near δ 20. The aromatic carbons of the 2-(arylazo)phenolate ligands are observed within δ 110–180, of which the most deshielded one (near δ 175) is assigned to the metallated carbon. The NMR spectral data are therefore in excellent agreement with the composition and stereochemistry of the complexes.

Infrared spectra of the complexes show many sharp and strong vibrations within 1600–200 cm⁻¹. Assignment of all these vibrations has not been attempted. However, a sharp vibration observed near 325 cm⁻¹ for all the complexes is assigned to the ν(Rh–Cl) stretch.[14] Each complex displays strong bands near 515, 690 and 740 cm⁻¹ which may be attributed to vibrations arising from the *trans*-Rh(PPh₃)₂ moiety as similar *trans*-M(PPh₃)₂ fragments are known to display such vibrations.[15] Comparison of the spectra of [Rh(PPh₃)₂(ap-R)Cl] complexes with the spectrum of [Rh(PPh₃)₃Cl] shows the presence of some new bands (*e.g.* vibrations near 810, 1250, 1300, 1360, 1425 and 1470 cm⁻¹) in the former complexes, which must be due to the coordinated 2-(arylazo)phenolate ligand.

The [Rh(PPh₃)₂(ap-R)Cl] complexes are soluble in common polar organic solvents such as acetonitrile, dichloromethane, acetone, *etc.*, producing intense greenish blue solutions except for [Rh(PPh₃)₂(ap-NO₂)Cl] which yields a green solution. Electronic spectra of all the complexes have been recorded in dichloromethane solution. Spectral data are presented in Table 3 and a selected spectrum is shown in Fig. 2. Each complex shows several intense absorptions in the visible region and two very intense absorptions in the ultraviolet region. The former absorptions are likely to be due to intra-ligand charge-transfer transitions taking place in the three-coordinated 2-(arylazo)phenolate ligand. Such intense absorptions are a familiar property of azo molecules, and are responsible for their usefulness in the dye industry. The absorptions in the ultraviolet region may be attributed to usual n $\longrightarrow$ π*, π $\longrightarrow$ π* transitions occurring within ligand orbitals.

Electron-transfer properties of the [Rh(PPh₃)₂(ap-R)Cl] complexes have been studied in dichloromethane solution (0.1 M NBu₄ClO₄) by cyclic voltammetry. All the complexes show an oxidative response to more positive potentials with respect to the SCE and a reductive response to negative ones. A representative voltammogram is shown in Fig. 3 and voltammetric data are presented in Table 3. Both the responses are believed to be centered on the coordinated 2-(arylazo)-

Table 3 Electronic spectral and cyclic voltammetric data

Compound	λ_{max}/nm (ε/M^{-1} cm^{-1})[a]	E/V vs. SCE[a,b]
[Rh(PPh$_3$)$_2$(ap-OMe)Cl]	630 (10500), 585 (9000), 535[c] (4300), 420[c] (3600), 380 (7000), 355 (17000), 290 (47300), 230 (60000)	0.65[d] (100),[e] −1.48[f]
[Rh(PPh$_3$)$_2$(ap-Me)Cl]	630 (8700), 610 (7600), 550[c] (4200), 385[c] (11500), 360[c] (18200), 290 (44500), 230 (59000)	0.76[d] (117),[e] −1.50[f]
[Rh(PPh$_3$)$_2$(ap-H)Cl]	630 (6600), 590 (2300), 355[c] (19700), 545[c] (3100), 290 (48500), 230 (6300)	0.81[d] (100),[e] −1.48[f]
[Rh(PPh$_3$)$_2$(ap-Cl)Cl]	650 (9500), 610 (8300), 560[c] (4000), 430[c] (2000), 390[c] (15000), 365[c] (23800), 300 (50700), 230 (84400)	0.84[d] (280),[e] −1.44[f]
[Rh(PPh$_3$)$_2$(ap-NO$_2$)Cl]	710 (11300), 650 (10200), 600[c] (5200), 420[c] (15200), 380[c] (25000), 305 (53800), 240 (102700)	1.10[d] (120),[e] −1.34[f]

[a] In dichloromethane. [b] Supporting electrolyte, NBu$_4$ClO$_4$. [c] Shoulder. [d] $E_{1/2} = 0.5 (E_{pa} + E_{pc})$ where E_{pa} and E_{pc} are anodic and cathodic peak potentials respectively. [e] $\Delta E_p = E_{pa} - E_{pc}$ in mV. [f] E_{pc} value.

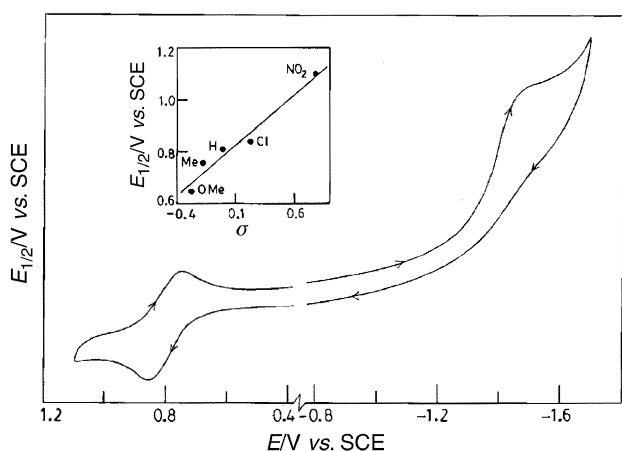**Fig. 3** Cyclic voltammogram of [Rh(PPh$_3$)$_2$(ap-H)Cl] in dichloromethane solution (0.1 M NBu$_4$ClO$_4$) at scan rate 50 mV s^{-1}. A least-squares plot of $E_{1/2}$ values of the rhodium(III)–rhodium(IV) couple versus σ is shown in the inset.

phenolate ligand. The oxidative response, observed within 0.65 to 1.10 V vs. SCE, is quasi-reversible in nature, characterized by a rather large peak-to-peak separation (ΔE_p) of 100–280 mV and the cathodic peak current (i_{pc}) is less than the anodic peak current (i_{pa}). The one-electron nature of this oxidation has been verified by comparing its current height (i_{pa}) with that of the standard ferrocene–ferrocenium couple under identical experimental conditions. This oxidation potential is found to be sensitive to the nature of the substituent (R) present in the 2-(arylazo)phenolate ligand increasing linearly (Fig. 3) with increasing electron withdrawing character (expressed in terms of the Hammett substituent constant) of the substituent [σ values of the substituents are: OMe −0.27, Me −0.17, H 0.00, Cl 0.23, NO$_2$ 0.78].[16] Though the degree of sensitivity of the oxidation potential to the nature of substituent is not very high, it is interesting here that a single substituent can influence the redox potentials in a predictable manner. The reductive response, displayed within −1.34 to −1.50 V vs. SCE, is irreversible in nature. The potential (E_{PC}) of this reduction does not show any systematic variation corresponding to variation in the nature of substituent R. The cyclic voltammetric studies thus show that these organometallic complexes of rhodium(III) are quite stable, while the oxidized and reduced complexes are not.

Conclusion

The present study shows that organometallic complexes of rhodium(III) can be synthesized without much difficulty by appropriate choice of the reactants, viz. the rhodium starting material and organic ligand. Generation of other organorhodium systems is in progress. These organorhodium complexes may be expected to exhibit interesting reactivities of

the Rh–C bond and such possibilities are currently under investigation.

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