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CYANOALKYL COMPLEXES OF PLATINUM(II)

IV*. NUCLEOPHILIC ATTACK ON THE CN GROUP BY AMINES

RENZO ROS**, JACQUES RENAUD*** and RAYMOND ROULET*

Institute of Inorganic and Analytical Chemistry, University of Lausanne, Place du Château 3, Lausanne (Switzerland)

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Summary

The nucleophilic addition of amines ($ArNH_2$, ArRNH, RR'NH) to the σ-coordinated CN group of *cis*-$[Pt(o\text{-}CH_2C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$ yields stable amidine complexes quantitatively. Precoordination of the nucleophile is the first step of the addition. The addition of NaN_3 to *cis*-$[Pt(CH_2C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$ gives the stable *cis*-$PtN_3(CH_2C_6H_4CN)(PPh_3)_2$ which on heating undergoes a 1,3 intramolecular cycloaddition to give the corresponding tetrazolate complex. Series of *trans* and *cis* influences of ligands were established, based on the ^1J(PtP) coupling constants of 40 cyanoalkyls and derivatives. No general correlations were found between ^1J(PtP) and the chemical shift δ(P), nor between ^1J and ^2J(PtCH).

Introduction

Investigations of the reactions of nitriles and of various ligands containing a CN group coordinated to transition metals have dealt mainly with their hydration to give carboxamides [1-4] and with the preparation of iminoether complexes [5]. In the previous parts of this series [6] we reported the preparation and spectroscopic properties of various cyanoalkyl complexes of the type $PtX(RCN)L_2$ and $[Pt(RCN)L_2]_2(BF_4)_2$ (R = $(CH_2)_nCN$, n = 1-3, o-$CH_2C_6H_4$; L = PPh_3, PPh_2Me, $AsPh_3$; X = Cl, Br) and the preparation of stable iminoether, iminothioether, amide and imide derivatives of the *o*-cyanobenzyl complexes [6c].

* For part III see ref. 6c.

** Present address: Facoltà di Chimica Industriale, Università di Venezia (Italy).

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TABLE 1

^1H AND ^{31}P NMR SPECTRAL DATA FOR PRODUCTS OF NUCLEOPHILIC ATTACK ON *o*-CYANOBENZYL—Pt(II) COMPLEXES

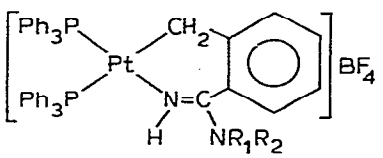
Complex		$\delta(CH_2)$ [a] (ppm)	^2J(PtCH) (Hz)	^3J(PPtCH) (Hz)	δ(others) (ppm)	δ(P) [c] (ppm)	^1J(PtP) [d] (Hz)	^2J(PP) (Hz)
I	*cis*-[Pt{$CH_2C_6H_4C(=NH)N(CH_3)_2$}$(PPh_3)_2$]$BF_4$	*b*	*b*	*b*	2.68s (NCH_3)	25.1d	1907	15
						16.4d	3974	
II	*cis*-[Pt{$CH_2C_6H_4C(=NH)N(C_2H_5)_2$}$(PPh_3)_2$]$BF_4$	*b*	*b*	*b*	2.91q (NCH_2)	23.9d	1855	15
					0.88t (CH_3)	16.5d	4024	
III	*cis*-[Pt{$CH_2C_6H_4C(=NH)N(CH_3)Ph$}$(PPh_3)_2$]$BF_4$	2.79q	65	6 (*cis*)	2.72s (NCH_3)	24.6d	1889	15
				8 (*trans*)		16.1d	4022	
IV	*cis*-[Pt{$CH_2C_6H_4C(=NH)NC_5H_{10}$}$(PPh_3)_2$]$BF_4$	*b*	62	*b*	2.75m (4H; α-CH_2)	25.2d	1900	15
					1.49m (6H; β, γ-CH_2)	16.2d	3958	
V	*cis*-[Pt{$CH_2C_6H_4C(=NH)NH(p\text{-}CH_3C_6H_4)$}$(PPh_3)_2$]$BF_4$	2.73q	66	6 (*cis*)	1.97s (*p*-CH_3)	23.7d	1843	15
				8 (*trans*)	8.30 (broad, C—NH)	17.2d	3990	
VI'	*cis*-[Pt{$CH_2C_6H_4C(=NH)NH(p\text{-}CH_3OC_6H_4)$}$(PPh_3)_2$]$BF_4$	2.75q	66	6 (*cis*)	3.75s (*p*-OCH_3)			
				9 (*trans*)	8.27 (broad, C—NH)			
VII	*cis*-[Pt{$CH_2C_6H_4CN$}$(NH_3)(PPh_3)_2$]BF_4	2.60q	77	6 (*cis*)	2.33 (broad, NH_3)	19.3d	1844	19
				11 (*trans*)		16.4d	4148	
VIII	*cis*-Pt($CH_2C_6H_4CN$)(phtalimido)$(PPh_3)_2$	2.73q	78	7 (*cis*)		23.1d	1945	16
				10 (*trans*)		14.0d	3708	
IX	*cis*-$PtN_3(CH_2C_6H_4CN)(PPh_3)_2$	2.63q	78	6 (*cis*)		19.9d	1813	16
				10 (*trans*)		19.5d	4062	
X	*cis*-Pt($CH_2C_6H_4CN_4$)$(PPh_3)_2$	2.53q	65	7 (*cis*)		23.1d	1891	14
				9 (*trans*)		17.5d	3974	

[a] In $CDCl_3$; TMS as internal standard. [b] Not observed. [c] In $CDCl_3$; positive sign for a resonance at lower field than 85% H_3PO_4 (external reference); $\delta(PPh_3)$ — 5.8 ppm. [d] Smaller ^1J for P *trans* to CH_2.

This paper deals with the nucleophilic attack by primary and secondary amines on the CN group of *cis*-$[Pt(o\text{-}CH_2C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$ to yield a new series of stable amidine complexes. N-substituted amidine complexes have been prepared by Wilkinson et al. [7] by treating primary aromatic amines with tetrachlorobis(alkanonitrile)rhenium(IV). Lebedinskii's "anomalous" amine—nitrile complexes of Pt^{II} [8] have been found since to be four coordinated compounds containing two amidine and two amine ligands $[Pt\{RC(NH)=NHR'\}_2(R'NH_2)_2]X_2$ [9].

Results and discussion

The complex *cis*-$[Pt(o\text{-}CH_2C_6H_4CN)(PPh_3)_2]_2(BF_4)_2$ obtained by reacting *trans*-$PtCl(CH_2C_6H_4CN)(PPh_3)_2$ with $AgBF_4$ has σ-coordinated CN groups very prone to nucleophilic attack [6]. New Pt^{II}—amidine complexes are quantitatively formed on stirring at room temperature a dichloromethane solution of the cationic *o*-cyanobenzyl dimer and an excess of a secondary amine (dimethylamine, complex I of Table 1; diethylamine, II; *N*-methylaniline, III; piperidine, IV) or of an aromatic primary amine (*p*-toluidine, V; *p*-anisidine, VI). These compounds are stable white chelates with an amidine group strongly bonded to platinum:



The formation of an amidine complex is clearly seen in the infrared by its ν(NH) band around 3300 cm^{-1} and two new bands in the ν(C=N) region around 1600 cm^{-1} while the ν(C≡N) around 2260 cm^{-1} disappears. The complexes were characterized by ^1H and ^{31}P NMR (Table 1), IR and Raman spectra and elemental analysis (Table 2). The proton decoupled ^{31}P spectra present an *AX* pattern with different ^1J(PtP) coupling constants, indicating that the two phosphines are *cis* to each other. When not hidden under other peaks, the observed methylene resonance is split into four lines of equal intensity by the two non-equivalent phosphorus (^3J(PPtCH) of Table 1) with satellites due to coupling with ^{195}Pt-(^2J(PtCH)). The amidine group is bonded through its imine nitrogen donor atom as no coupling was observed between ^{195}Pt and the N—CH_3 protons of complexes I and III. Mastin [10] has proposed an assignment of the *cis* and *trans* stereochemistry in bis(triphenylphosphine)platinum(II) complexes based on the relative intensity of an IR and Raman band at ca. 550 cm^{-1}. This band was found to be very strong in the infrared (weak in Raman) of *cis* complexes and weak in the infrared (strong in Raman) of *trans* compounds. Mastin's rule holds without exceptions for the 38 complexes reported in this series, which had their stereochemistry unambiguously assigned by ^{31}P NMR.

The first step of the addition is probably the coordination of the nucleophile HY to platinum. The equilibrium of eqn. 1 is completely shifted to the

$$cis\text{-}[Pt(CH_2C_6H_4CN)(PPh_3)_2]_2^{2+} + 2HY \rightleftharpoons 2cis\text{-}[Pt(CH_2C_6H_4CN)(HY)(PPh_3)_2]^+ \quad (1)$$

TABLE 2

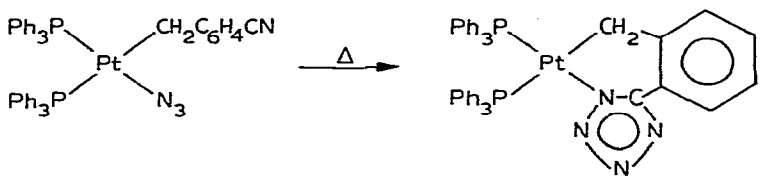
ANALYTICAL, IR AND RAMAN SPECTRAL DATA

Complex	M.p. (dec.) (°C)	Analysis found (calcd.) (%)				ν(NH) (cm^{-1})	ν(C≡N) region (cm^{-1})	Band at 550 ± 5 cm^{-1} [a]	Others
		C	H	N	F				
I	215-219	56.60	4.45	3.01	8.02	IR 3348w	1582s, 1550s	IR 546s	1055 $\nu(BF_4)$ [b]
		(57.08)	(4.48)	(2.89)	(7.85)	R 3350vw		R 550vw	
II	200-215	57.23	4.74	2.91		3350w	1575s, 1540s	IR 545s	1050 $\nu(BF_4)$
		(57.89)	(4.76)	(2.81)					
III	263-266	59.23	4.33	2.76	7.60	3335, 3360w	1578s, 1543s	IR 549s	1055 $\nu(BF_4)$
		(59.47)	(4.40)	(2.72)	(7.38)				
IV	238-244	57.70	4.83	3.03		3375w	1580s, 1548s	IR 548s	1055 $\nu(BF_4)$
		(57.79)	(4.70)	(2.78)					
V	262-267	59.22	4.26	2.83	7.54	3330sh, 3315w	1585s, 1541vs	IR 548s	1060 $\nu(BF_4)$
		(59.47)	(4.40)	(2.72)	(7.38)		1612m, 1510m		
VI	265-270	57.98	4.60	2.79		3300 broad	1581m, 1539s	IR 546s	1063 $\nu(BF_4)$
		(58.57)	(4.34)	(2.68)			1607m, 1504m	R 550vw	
VII	215-220	56.40	4.52	2.98	8.11	3350w, 3320w	1617sh, 1607m	IR 550s	2218m ν(C≡N)
		(56.24)	(4.18)	(2.98)	(8.09)	3250w, 3175vw	1593m, 1586m	R 550w	IR 1063 $\nu(BF_4)$
VIII	189-193	63.39	4.34	2.80			1655s (CO)	IR 546s	IR 2220m ν(C≡N)
		(63.59)	(4.11)	(2.85)			1630m	R 548s [c]	R 2218m
IX	224-226	60.29	4.10	6.29				IR 546s	IR 2218m ν(C≡N) R 2215m
		(60.19)	(4.13)	(6.38)				R 547m	IR 2058vs $\nu(N_3)_{as}$ R 2053w
									IR 1278m $\nu(N_3)_s$ R 1279m
X	247-249	60.26	4.11	6.48				IR 548s	
		(60.19)	(4.13)	(6.38)				R 550vw	

[a] Mastin's identification method [10] of isomers of $Pt(PPh_3)_2XY$; the band should be strong in IR and weak in Raman for *cis* and the reverse for *trans*. [b] vs, broad.
[c] Band of free phthalimide appear in that region.

right at room temperature for HY = NH_3, $MeNH_2$, but it favours the dimer in the case of HY = MeOH [6c]. Only the substituted product *cis*-[$Pt(CH_2C_6H_4CN)(NH_3)(PPh_3)_2$]$BF_4$ (VII) was obtained by bubbling ammonia through a warm solution of the cationic dimer in dichloromethane. With monoethylamine a mixture of the substituted product and of the corresponding amidine complex was obtained and could not be separated. With pyrrole the mixture apparently contained *cis*-[$Pt\{CH_2C_6H_4C(=NH)NC_4H_4\}(PPh_3)_2$]$BF_4$ (δ(P) 11.8 ppm with ^1J(PtP) 3750 Hz and 22.6 ppm with ^1J(PtP) 1920 Hz for the phosphorus *trans* to CH_2), and *trans*-[$Pt(CH_2C_6H_4CN)(HNC_4H_4)(PPh_3)_2$]$BF_4$ (δ(P) 26.1 ppm, ^1J(PtP) 3070 Hz, ν(CN) 2220 cm^{-1}).Pyrrole thus seems to catalyse the *cis—trans* isomerisation of the product derived from the substitution reaction.

We have observed one case where the precoordination of the nucleophile is clearly the first step of the attack of the CN group: the addition of NaN_3 in excess to a suspension of *cis*-[$Pt(CH_2C_6H_4CN)(PPh_3)_2$]$_2(BF_4)_2$ gives the stable *cis*-$PtN_3(CH_2C_6H_4CN)(PPh_3)_2$ (IX), but a 1,3 intramolecular cycloaddition takes place upon refluxing a solution of IX in acetone, giving the corresponding tetrazolate complex X:



Cyclisation was not observed on heating the isomer *trans*-$PtN_3(CH_2C_6H_4CN)(PPh_3)_2$ [6b]. Beck et al. [11] have previously obtained tetrazolate palladium(II) complexes by treating *trans*-$Pd(N_3)_2(PPh_3)_2$ with a variety of nitriles, and tetrazolate platinum(II) with σPt—C bonds by treating *cis*-$Pt(N_3)_2(PPh_3)_2$ with isonitriles. Treichel et al. [12] have identified a 5-metalo-1-methyl-1,2,3,4-tetrazole complex as the product of the reaction of [$Pt(CNCH_3)_2$(diphos)]$(PF_6)_2$ with azide.

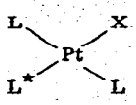
Imides are much weaker bases and their addition to the nitrile group was unsuccessful. For example, phtalimide gave no reaction while adding its potassium salt to the dimer caused the Pt—NC bridge splitting, giving *cis*-$Pt(CH_2C_6H_4CN)\{N(CO)_2C_6H_4\}(PPh_3)_2$ (VIII).

^{31}P *NMR data and the trans influence*

The *trans* influence has been defined as the extent to which a given ligand L weakens the M—L′ bond *trans* to it in the fundamental state of the complex. The expression for ^1J(PtP) given by Pidcock et al. [13] showed that smaller coupling constants were associated with platinum—phosphorus bonds of lower *s*-character; in platinum—phosphine compounds a small ^1J should indicate that the ligand in *trans* position to the phosphine has a high *trans* influence. This has been used to establish a sequence of *trans* influences, and the NMR sequence has been compared in a recent review with those obtained by different methods [14]. We can use the NMR data of the 48 compounds prepared in this series [6] to locate the cyanoalkyls and their derivatives in the sequence of *trans* influence; six-membered ring chelates are included, and we assume that the platinum

TABLE 3

^1J(PtP) COUPLING CONSTANTS

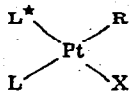


(L = L* = PPh_3)

X	^1J(PtP*) (Hz)	Ref.
$\underline{C}H_2CN$	2210	6a
$\underline{C}H_2C_6H_4CN$	1865	6b

X	^1J(PtP) (Hz)	Ref.
$\underline{C}H_2CN$	2695	6a
$\underline{C}H_2C_6H_4CN$	2850	6b

(R = *o*-cyanobenzyl and chelated derivatives; the coordinated atom is underlined; N_4C = tetrazole; $N(CO)_2C_6H_4$ = phtalimide)



X	^1J(PtP*) (Hz)	Ref.
PPh_3	2850	6b
$\underline{N}HCOC_6H_4$—	3579	6c
$\underline{N}(CO)_2C_6H_4$	3708	this work
$\underline{N}_4CC_6H_4$—	3974	this work
$H\underline{N}{=}C(NMe_2)C_6H_4$—	3974	this work
$H\underline{N}{=}C(OMe)C_6H_4$—	4010	6c
$H\underline{N}{=}C(SMe)C_6H_4$—	4055	6c
$\underline{N}_3$	4062	this work
NH_3	4148	this work
Br	4350	6b
Cl	4360	6b
$\underline{N}CC_6H_4$—	4450	6b
$H_2\underline{N}COC_6H_4$—	4840	6c

square planar geometry is not distorted. The results for the *cis* complexes are summarized in Table 3.

The sequence of *trans* influence is: —$\underline{C}_3H_6CN$ [6a] > —$\underline{C}H_2C_6H_4CN$ > —$\underline{C}H_2CN$ > PPh_3 > —$\underline{N}HCOC_6H_4$— > phtalimide > tetrazole ~ $H\underline{N}{=}C(NMe_2)$-$C_6H_4$— > $H\underline{N}{=}C(OMe)C_6H_4$— > $H\underline{N}{=}C(SMe)C_6H_4$— > N_3 > NH_3 > Br > Cl > $\underline{N}CC_6H_4$— > $H_2\underline{N}COC_6H_4$—.

The order imide > imine > azide > amine > nitrile > amide follows the order of decreasing electron density on nitrogen. For the imine complexes reported, the sequence NMe_2 > OMe follows also the order of decreasing inductive effect $+I_s$ of the substituents.

The *trans* influence of alkyl is higher than that of phosphine; this order has been observed previously for other Pt^{II} complexes [15].

Similarly the following sequence of *cis* influence is deduced from the ^1J(PtP) coupling constants of the *trans* complexes [6]: CNAr > $NCCH_3$ > PPh_3 > N_3 > Br > Cl > —$\underline{C}H_2CN$ > —$\underline{C}H_2C_6H_4CN$ > —$\underline{C}H_2CH_2CN$ > —$\underline{C}H_2CH_2$-CH_2CN > —$\underline{C}OCH_2C_6H_4CN$ > —$\underline{C}OCH_2CH_2CH_2CN$.

The ^{31}P resonance of a coordinated phosphine always appeared at lower field than that of the free phosphine. When comparing 14 *trans*-bis(triphenylphosphine) complexes, we found no general relation between the chemical shift δ(P) and ^1J(PtP): indeed, a linear relation holds only approximately for 11 compounds (Fig. 1). Such a correlation was shown to exist in *trans*-$PtHX(PEt_3)_2$ complexes [16]. There was no correlation either between ^1J(PtP) and the coupling constant ^2J(PtCH) of the methylene protons in *trans* position to phosphorus in the 19 *cis* complexes of *o*-cyanobenzyl reported in [6] and in this work.

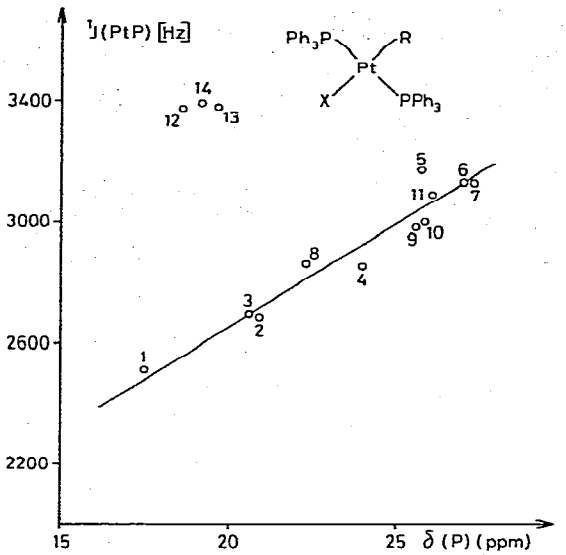


Fig. 1. Plot of ^1J(PtP) vs. δ(P) for complexes *trans*-PtR(X)$(PPh_3)_2$ (R = CH_2CN 1-4; C_2H_4CN 5; C_3H_6CN 6,7; $CH_2C_6H_4CN$ 8-11; $COCH_2C_6H_4CN$ 12, 13; COC_3H_6CN 14; X = ArNC 1; CH_3CN 2; PPh_3 3, 8; Cl 4, 6, 11, 13; Br, 5, 7, 10, 12, 14; N_3 9).

Experimental

The spectroscopic techniques were described earlier [6]. Dornis und Kolbe (Mulheim) carried out the microanalyses.

Preparation of complexes

cis-[Pt{$CH_2C_6H_4C(=NH)NMe_2$}$(PPh_3)_2$]BF_4 (I)

Dimethylamine was bubbled through a solution of 1 g *cis*-[Pt$(CH_2C_6H_4CN)$-$(PPh_3)_2$]$_2(BF_4)_2$ [1] (A) in dichloromethane (20 ml). The solution was evaporated and the dry residue extracted with acetone; I was precipitated by adding ether, and was reprecipitated from CH_2Cl_2/ether as a white powder. Yield 65%.

cis-[Pt{$CH_2C_6H_4C(=NH)NEt_2$}$(PPh_3)_2$]BF_4 (II)

A (0.5 g) was stirred with Et_2NH (1 ml) in CH_2Cl_2 (10 ml) for 4 h. The volume was reduced to 5 ml and the white complex precipitated with ether. Yield 75%. The same reaction with $EtNH_2$ gave a mixture of two cationic complexes which could not be separated by fractional crystallization. The reaction with pyrrole gave the mixture described in the text (the compounds were not analyzed). A did not react with diphenylamine.

cis-[Pt{$CH_2C_6H_4C(=NH)N(CH_3)C_6H_5$}$(PPh_3)_2$]$BF_4$ (III)

A (0.5 g) and *N*-methylaniline were heated at 50°C in acetone (20 ml) for 20 h. III was precipitated by adding ether and was recrystallized from CH_2Cl_2/pentane. Yield 80%.

cis-[Pt{$CH_2C_6H_4(=NH)NC_5H_{10}$}$(PPh_3)_2$]$BF_4$ (IV)

A (0.5 g) was stirred with piperidine (0.6 ml) in acetone (20 ml) for 2 h

at 50°C, then 10 h at room temperature. The volume was reduced to 5 ml and IV precipitated by adding ether. Yield 90%.

cis-[Pt{$CH_2C_6H_4C(=NH)NH(p\text{-}CH_3C_6H_4)$}$(PPh_3)_2$]$BF_4$ (V) and cis-[Pt-{$CH_2C_6H_4C(=NH)NH(p\text{-}CH_3OC_6H_4)$}$(PPh_3)_2$]$BF_4$ (VI)

A (0.5 g) was stirred overnight in acetone (20 ml) with a threefold excess of *p*-toluidine or *p*-anisidine respectively, at room temperature. The volume was reduced to 5 ml, the complex was precipitated by adding ether, and was recrystallized from CH_2Cl_2/pentane. Yield 80%.

cis-[Pt($CH_2C_6H_4CN$)(NH_3)$(PPh_3)_2$]BF_4 (VII)

A (0.4 g) was stirred in CH_2Cl_2 (15 ml) for 3 h under an atmosphere of dry ammonia. The volume was reduced to 5 ml and the white complex precipitated by adding ether. Yield 75%.

cis-Pt($CH_2C_6H_4CN$){$N(CO)_2C_6H_4$}$(PPh_3)_2$ (VIII)

A (0.5 g) was stirred with potassium phtalimide (0.1 g) in CH_2Cl_2 (25 ml) for 2 h. The filtrate was evaporated to dryness, washed with water, then with hexane. Yield 90%.

cis-PtN_3($CH_2C_6H_4CN$)$(PPh_3)_2$ (IX) and cis-Pt($CH_2C_6H_4CN_4$)$(PPh_3)_2$ (X)

NaN_3 in excess was added to a suspension of A in acetone. The volume was reduced by half and the white powder washed with methanol. Yield of IX 95%. IX (0.4 g) was heated under reflux in acetone (20 ml) for 5 h. The volume was reduced to 5 ml and the white microcrystalline powder was washed with methanol. Yield of X 95%.

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