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PALLADIUM ASSISTED ORGANIC REACTIONS

VI *. A NEW METHOD FOR THE PREPARATION OF CYCLOPALLADATED BENZALIMINES

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Summary

A new, improved method is described for the preparation of cyclopalladated benzalimines; it consists of reacting the *ortho*-bromobenzalimine with bis(dibenzylideneacetone)palladium(0). A number of substituted *o*-bromobenzalimines has been studied; the bridged bromide dimers and the corresponding bromo(*N*-substituted benzalimine-6,*C*,*N*)triphenylphosphinepalladium(II) complexes have been fully characterised and ^{1}H and ^{13}C NMR spectral data recorded. In the cases of the *N*-phenylbenzalimines studied, bis(triphenylphosphine) complexes were also isolated and characterised.

Introduction

The preparation and properties of chelated nitrogen- and phosphorus-containing ligands by cyclometallation reactions with transition metal complexes has become an important aspect of organometallic chemistry [2–4]. Recent interest has focused upon cyclopalladated benzylamine, benzalimine and azobenzene derivatives [1,6–14] since insertions into the carbon–palladium bond have been found to be facile [5]. Because of this, and because of the regiospecific nature of the cyclopalladation reaction itself, a new strategy in organic synthesis is being developed by us [1,10,13–15] and by others [8,11,12]. Using benzalaniline as a masked benzaldehyde, Murahashi et al. [16] described the preparation of a number of *ortho*-alkylbenzaldehydes by reacting cyclopalladated benzalaniline with a Grignard reagent, followed by hydrolysis. Girling and Widdowson [12] have successfully utilised a number of cyclopalladated *N*-t-butylbenzalimines in the synthesis of some isoquinoline derivatives. Under the usual conditions for the preparation of the cyclopalladated ben-

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zalimines [17,18], methanolysis or hydrolysis of the C=N bond can become a significant side reaction, so we have developed a new synthetic procedure which can give high yields of the required cyclopalladated benzalimines [19], and we present in this paper the first comprehensive ^1H and ^{13}C NMR spectral study of such complexes.

Experimental

The benzalimines were obtained from the corresponding *ortho*-bromobenzaldehyde and the appropriate primary amine under standard conditions; purity was checked by GC-MS. Palladium chloride, loaned by Johnson-Matthey, was used without further purification. The bis(dibenzylideneacetone)palladium(0) was prepared as described by Rettig and Maitlis [20]. ^1H NMR spectra were recorded using a Bruker CXP-300 spectrometer operating at 300 MHz, and ^{13}C NMR spectra were obtained at 75.4 MHz. All NMR spectra were recorded on compounds in $CDCl_3$ solution at ambient probe temperature; chemical shifts in ppm refer to internal TMS as standard. GC-MS data were obtained with a Carlo-Erba GC linked to a Kratos MS25 mass spectrometer. Molecular weights of the imines were taken as the parent ions in the mass spectra, whereas those of the palladium complexes were computed from vapour pressure osmometry of samples dissolved in chloroform. Microanalyses were performed by the University of Queensland Microanalytical Laboratory and the Australian Microanalytical Service, Melbourne.

Preparation of the di-μ-bromobis(N-substituted-benzalimine-6,C,N)dipalladium(II) complexes

These were all prepared by the same general procedure, illustrated below for di-μ-bromobis(*N*-methyl-3,4-dimethoxybenzalimine-6,*C*,*N*)dipalladium(II) (**2a**). *N*-Methyl-3,4-dimethoxy-6-bromobenzalimine (0.80 g, 3.10 mmol) was added to a stirred solution of bis(dibenzylideneacetone)palladium(0) (1.60 g, 2.79 mmol) in dry benzene (150 ml) at room temperature under nitrogen. The solution was heated slowly to about 60°C, at which temperature the reaction occurred quickly, and the colour changed dramatically from deep purple to a yellow-green. The yellow colour of the palladium(II) complex was discoloured by some palladium metal. The solution was heated for another 5 min, then cooled to room temperature when the insoluble complex was collected, washed with benzene and dried to yield 0.96 g of complex (96%).

All of these dimeric complexes, except for di-μ-chlorobis(*N*-t-butylbenzalimine-2,*C*,*N*)dipalladium(II) (**2m**), were too insoluble to characterise fully. The complex **2m** has been described by Girling and Widdowson [12] in a preliminary publication. Our sample analysed as C, 49.2; H, 5.1; N, 4.1; Cl, 10.6. $C_{28}H_{34}Cl_2N_2Pd_2$ calcd.: C, 49.3; H, 5.0; N, 4.1; Cl, 10.4% (contains 1 mol of benzene of crystallisation).

All complexes where characterised as the bromo(*N*-substituted-benzalimine-6,*C*,*N*)triphenylphosphinepalladium(II) monomeric complexes (**3**), which were prepared by reacting the above dimers with triphenylphosphine. Pure monotriphenylphosphine complexes of the *N*-phenyl compounds were best obtained by using a ratio of triphenylphosphine to dimeric complex of less than 2/1. The preparation of bromo(*N*-methyl-3,4-dimethoxybenzalimine-6,*C*,*N*)triphenylphosphinepalladium(II) (**3a**) is typical. Triphenylphosphine (0.32 g, 1.22 mmol) and di-μ-

bromobis(*N*-methyl-3,4-dimethoxybenzalimine-6,*C*,*N*)dipalladium(II) (**2a**) (0.40 g, 0.55 mmol) were stirred at room temperature in methylene chloride (ca. 20 ml). The resulting yellow solution was filtered through celite to remove any palladium metal. The filtrate was then heated, and methanol added to crystallise the complex. After cooling, the complex was separated by filtration, washed with methanol and dried to yield 0.65 g of product (95%).

The analytical data for all of the complexes prepared are summarised in Table 1.

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TABLE 1

ANALYTICAL DATA

Compound	Molecular formula	Found (calcd.) (%)				Mol. wt. Found (Calcd.)	Yield [a] (%)
		C	H	N	X		
3a	$C_{28}H_{27}BrNO_2PPd$	53.6 (53.7)	4.35 (4.2)	2.2 (2.2)	12.7 (12.8)	585 (627)	95 (96)
3b	$C_{33}H_{29}BrNO_2PPd$	57.4 (57.5)	4.4 (4.2)	1.9 (2.0)	11.4 (11.6)		78 (100)
3c	$C_{34}H_{31}BrNO_2PPd$	58.0 (58.1)	4.5 (4.45)	1.9 (2.0)	11.5 (11.4)		95 (68)
3d	$C_{36}H_{35}BrNO_4PPd$	56.2 (56.7)	4.6 (4.6)	1.6 (1.8)	10.2 (10.5)		84 (95)
3e	$C_{35}H_{33}BrNO_3PPd$	57.1 (57.4)	4.1 (4.5)	1.8 (1.9)	10.9 (10.9)		82 (92)
3f	$C_{31}H_{34}BrNO_2PPd$	55.3 (55.6)	4.9 (5.1)	1.8 (2.1)	11.9 (11.9)		91 (94)
3g	$C_{27}H_{23}BrNO_2PPd$	53.6 (53.1)	3.8 (3.8)	2.3 (2.3)	12.9 (13.1)		88 (89)
3h	$C_{32}H_{25}BrNO_2PPd$	56.9 (57.1)	3.9 (3.75)	2.0 (2.1)	11.7 (11.9)		95 (83)
3i	$C_{27}H_{25}BrNOPPd$	53.9 (54.3)	4.8 (4.2)	2.1 (2.35)	13.0 (13.4)		85 (97)
3j	$C_{32}H_{27}BrNOPPd$	58.3 (58.3)	4.3 (4.1)	2.0 (2.1)	11.8 (12.1)		63 (88)
3k	$C_{26}H_{23}BrNPPd$	55.2 (55.1)	4.0 (4.1)	2.3 (2.5)	13.4 (14.1)		85 (41)
3l	$C_{31}H_{25}BrNPPd$	59.2 (59.0)	4.1 (4.1)	2.2 (2.2)	12.7 (12.9)		88 (98)
3m	$C_{29}H_{29}ClNPPd$	61.1 (61.7)	5.1 (5.2)	2.2 (2.5)	6.1 (6.3)	540 (564)	57
4b	$C_{51}H_{44}BrNO_2P_2Pd$	64.5 (64.4)	4.7 (4.7)	1.3 (1.5)	8.5 (8.4)	476 [b] (951)	75
4h	$C_{50}H_{39}BrNO_2P_2Pd$	64.3 (64.3)	4.4 (4.2)	1.4 (1.5)	8.7 (8.6)		89
4j	$C_{50}H_{42}BrNOP_2Pd$	65.0 (65.2)	4.7 (4.6)	1.4 (1.5)	9.0 (8.7)		51
4l	$C_{49}H_{40}BrNP_2Pd$	66.2 (66.0)	4.65 (4.5)	1.4 (1.6)	9.0 (9.0)		75
2m	$C_{28}H_{34}Cl_2N_2Pd_2$	49.2 (49.3)	5.1 (5.0)	4.1 (4.1)	10.6 (10.4)	575 (604) [c]	95

[a] Yields of parent dimer given in parentheses. [b] Dissociates in solution. [c] Mol. wt. less benzene.

TABLE 2

^{1}H NMR SPECTRAL DATA (δ in ppm, J in Hz)

Compound	H(2)	H(5)	CH=N	C(3)–OMe	C(4)–OMe	Other	
3a	6.83	5.92(d) J(PH) 5 41	8.04(d) J(PH) 6.43	3.77	2.84	CH_3 3 82	
3b	6.95	6.01(d) J(PH) 6.50	8.14(d) J(PH) 7 01	3.78	2.89		
3c	6.73	5.94(d) J(PH) 6.43	[a]	3.69	2 83	CH_2 5.34	
3d	6.76	5.95(d) J(PH) 6.44	7.85 J(PH) 8.06	3.68	2.84	CH_2 5.28 2 × OMe 3.85	
3e	6.73	5.94(d) J(PH) 6.39	[a]	3.67	2.82	CH_2 5 28 OMe 3.76	
3f	6.87	5.98(br)	8.12(br)	3.76	2.86	CH_3 1.67	
3g	6.75	5.87(d) J(PH) 6.01	7.95(dq) J(PH) 8.04 J(HH) 1 37			CH_3(dd) 3.77 J(PH) 2.07 J(HH) 1 37	
3h	6.89	5.96(d) J(PH) 6 09	8.09(d) J(PH) 6.82			O–CH_2–O 5 72	
3i	6.84(d) J(HH) 2 86	6.24(d) J(PH) 5.88 J(HH) 8.57	8.10(dq) J(PH) 7.8 J(HH) 1.42	3.62		H(4) 6.13(dd) J(HH) 8.57 J(HH) 2.86	CH_3 3.85(d) J(HH) 1.42

3j	6.98(d) J(HH) 2.61	6.34(dd) J(PH) 6.15 J(HH) 8.56	8.22(d) J(PH) 6.74	3.66		H(4) 6.23(dd) J(HH) 8.58 J(HH) 2.48		
3k	7.24(dd) J(HH) ~ 7.5 J(HH) 1.51	6.40(br)	8.14(br)			CH_3 3.87	H(3) 6.89(dt) J(HH) ~ 7.50 J(HH) 1.01	H(4) 6.52(dt) J(HH) ~ 7.50 J(HH) 1.50
3l	7.25(d) [b]	6.46(t) [b]	8.25(d) J(PH) 6.78				H_3 6.89(t) [b] H_4 6.62(t) [b]	
3m	6.85(m) [b]	6.45(m)	8.18 [c]			CH_3 1.62		
4b	6.78(br)	6.14	8.56(br)	3.72	3.17			
4h	6.60(br)	6.30	8.55(br)			O–CH_2–O 5.62		
4j	6.84(br,d)	6.52(br)	8.30	3.60		H(4) 6.16(dd) J(HH) 8.38 J(HH) 2.96		
4l	[a]	~ 6.5	8.14					
2m	7.48(dd) J(HH) 7.31 J(HH) 1.28	7.21(dd) J(HH) 6.69 J(HH) 2.13	7.87			CH_3 1.54	H(3), H(4) 7.02(m)	

[a] Resonance under Ph_3P protons. [b] Assignment uncertain. [c] No visible P coupling.

TABLE 3

^{13}C NMR SPECTRAL DATA (δ in ppm, J (Hz) in parentheses)

Compound	Aromatic								Triphenylphosphine				Other			
	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	CH=N	OMe	C(1)	C(2,6)	C(3,5)	C(4)				
3a	139.7	110.3	145.6	148.8 (5.7)	121.5 (12.0)	152.9	175.2	55.9 55.1	131.8 (51.2)	135.5 (12.1)	128.1 (10.0)	130.8	CH_3	49.6		
3b	139.9	111.4	145.8	149.8 (6.9)	121 4 (11.4)	154.2	175 3	55.8 55.0	131.9 (51.2)	135.5 (11.9)	128.1 (11.1)	130 9	Ph*-N Ph	150.2 Ph 127.9 Ph		126.7 124 0
3c	140.0	110.8	145.7	149.0 (6.5)	121.4 (11.9)	152.8	174.9 (3.7)	55 9 55.2	131.9 (50.2)	135.5 (12.1)	128.1 (10.9)	130.8	Ph*-CH_2 Ph	137.7 Ph 129.8 Ph Ph-CH_2*		128.7 127.6 62.3
3d	140.0	110.8	145.7	148.9 (6.2)	121.4 (12.1)	152.6	174.4 (3.9)	56.1 56.0 55.9 55.1	131.9 (50.3)	135.5 (12.0)	128.1 (10.9)	130.8	Ph*-CH_2 Ph*-OMe Ph*-OMe	130.1 Ph 149.3 Ph 148.7 Ph-CH_2*		122.2 113.5 62.3
3e	140.1	110.7	145.6	148.8 (6.4)	121.4 (12.0)	152.5	174.4 (3.5)	55.8 55.2 55.0	131.9 (50.1)	135.5 (11.9)	128.0 (10.9)	130.8 (1.8)	Ph*-CH_2 Ph	129.5 Ph*-OMe 131.2 Ph Ph-CH_2*		159.2 114.2 61.9
3f	140.1	110.8	145.7	148.3 (7.6)	121 2 (12.0)	151.5	169.0	55.9 55.1	132.3 (51.0)	135.4 (11.7)	128.0 (10.7)	130.6	C*$(CH_3)_3$ $C(CH_3*)_3$	62.6 30.2		
3g	140.1	107.4	144.3	147.6 (7.1)	117.9 (11.8)	155.0	174.9		131.5 (50.2)	135 4 (11.8)	128.1 (10.7)	130.8	O-CH_2-O CH_3	100.6 49.8		
3h	140.3	108.6	144.5	148.7 (7 2)	117.9 (11.1)	156.7	174.8		131.6 (51.5)	135.4 (11.8)	128.1 (11.4)	130 8	O-CH_2-O Ph*-N Ph	100.8 Ph 150.1 Ph 127.9		126.7 124.0

3i	149.1	113.3	148.3	115.1 (5.4)	138.4 (11.6)	156.5	175.9	55.1	131.8 (51.1)	135.5 (12.1)	128.0 (10.3)	130.7	CH_3	49.9		
3j	150.1	114.4	148.0	116.5 (5.1)	138.6 (10.0)	156.7	176.1	55.2	131.9 (52.4)	135.5 (12.0)	128.0 (10.0)	130.7	Ph*–N Ph	156.7 Ph 127.9 Ph		127.0 123.9
3k	148.0	129.6	127.4	124.1	137.8	159.0	176.2		131.7 (50.2)	135.4 (11.9)	128.0 (11.5)	130.7	CH_3	49.9		
3l	148.0	128.9	126.8	123.7	137.9 (10.0)	159.9	176.2		131.7 (51.5)	135.3 (12.1)	127.8 (9.8)	130.5	Ph*–N Ph	149.9 Ph 127.8 Ph		124.1 123.7
3m	157.1	138.1	129.0	148.6	123.9	134.5	169.6		131.6 (51.3)	135.5 (11.8)	127.9 (11.0)	130.5	$C^*(CH_3)_3$ $C(CH_3^*)_3$	62.9 29.8		
4b	[a]	112.4	146.2	150.2	119.1	155.3	~167		131.9	134.7	127.9	129.9	Ph*–N Ph	152.3 Ph 128.6 Ph		125.3 122.0
4h	[a]	109.2	144.8	148.6	115.4	158.5	164.5	56.1 55.2	131.4	134.6	127.9	129.9	O–CH_2–O Ph*–N Ph	100.1 Ph 152.6 Ph 128.8		125.1 121.5
4j	[a]	115.7	152.0	117.6	136.9	156.9	~167	55.5	131.8	134.8	127.8	129.8	Ph*–N Ph	152.3 Ph 128.8 Ph		125.5 121.7
4l	132.0 [b]	122.8 [b]	[a]	134.5 [b]	***a***	136.7	[a]		131.6	134.7	127.8	129.7	Ph*–N Ph	152.0 Ph 128.8 Ph		127.9 121.8
2m	146.6	129.2	128.3	127.4	124.7	133.5	165.8						$C^*(CH_3)_3$ $C(C^*H_3)_3$	62.4 29.3		

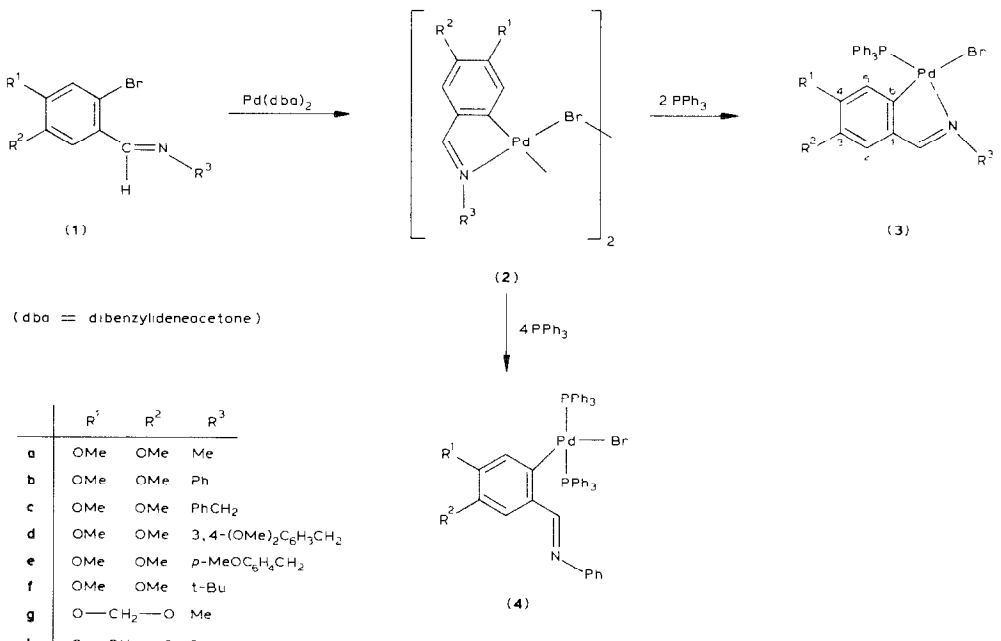
[a] Not visible. [b] Not unequivocably assignable.

Preparation of the bis(triphenylphosphine) complexes

These were prepared by treating an excess of triphenylphosphine with the dimeric *N*-phenylbenzalimine complexes (**2**) in a method essentially similar to that used for the monotriphenylphosphine complexes. Analytical data are shown in Table 1.

Results and discussion

Our method of synthesis of cyclopalladated benzalimines involves the coordination, and subsequent oxidative addition, of the required *ortho*-halogenated benzalimine (**1**) to bis(dibenzylideneacetone)palladium(0) (see Scheme 1). The best procedure is to add the reagents together at room temperature, in a solution of benzene, and then heat slowly to 50–60°C when the reaction proceeds quickly, and with very little decomposition. All of the dimeric complexes **2** prepared in this way contained a small amount of palladium metal. Although three of these complexes, **2m**, **2k** and **2l** have been prepared before [12], none had been fully characterised, due mainly to their low solubility. However, we have been able to characterise di-μ-chlorobis(*N*-t-butylbenzalimine-2,*C*,*N*)dipalladium(II) (**2m**). It is dimeric in solution showing a C=N stretching frequency at 1602 cm^{-1}, compared with 1631 cm^{-1} for the C=N group in the free ligand (**1m**). For the other dimeric complexes of type **2** ν_{max} fell in



	R^1	R^2	R^3
a	OMe	OMe	Me
b	OMe	OMe	Ph
c	OMe	OMe	$PhCH_2$
d	OMe	OMe	3,4-$(OMe)_2C_6H_3CH_2$
e	OMe	OMe	*p*-$MeOC_6H_4CH_2$
f	OMe	OMe	t-Bu
g	O—CH_2—O		Me
h	O—CH_2—O		Ph
i	H	OMe	Me
j	H	OMe	Ph
k	H	H	Me
l	H	H	Ph
m	H	H	t-Bu

(Cl in place of Br)

SCHEME 1

the range 1601–1610 cm^{-1}. In the ^1H NMR spectrum of **2m** the imine and t-butyl hydrogens resonate at δ 7.87 and 1.54 ppm, respectively, compared with 8.68 and 1.31 ppm in the ligand **1m**. Similarly, in the ^{13}C NMR spectrum of **2m**, the imine carbon, the $C^*(CH_3)_3$ and the $C(C^*H_3)_3$ atoms absorb at δ 168.8, 62.4 and 29.3 ppm, respectively, while in the benzalimine **1m** these occur at δ 152.1, 57.9 and 29.7 ppm respectively. The chemical shift of the Pd–C^* appears, slightly broadened, at 133.5 ppm; the only other quaternary carbon atom is then assigned to the peak at 146.6 ppm. The structure of the complex is thus established as **2m**. By inference, the structures of the other dimeric complexes are assigned as **2a**–**2l**.

The formation of these cyclopalladated dimers seem to occur more readily with the *ortho*-bromo- than with the *ortho*-chlorobenzalimines since, although the reaction between the palladium(0) complex and **1a** proceeded smoothly, the corresponding reaction with *N*-methyl-3,4-dimethoxy-6-chlorobenzalimine resulted only in decomposition. Additionally, the cyclopalladation reaction appears to be dependant upon the steric nature of the benzalimine; the bulkier $N-R_3$ is in the benzalimine **1**, the more readily reaction occurs. Thus, although the reaction involving *N*-methyl-3,4-dimethoxy-6-chlorobenzalimine resulted in decomposition, that with the corresponding *N*-t-butyl derivative **1m** gave a clean product in high yield.

The complexes **2g** and **3g** prepared by this method are, of course, isomeric with the complexes prepared by cyclopalladation of *N*-methyl-3,4-methylenedioxybenzalimine [21].

For ease of characterisation the dimeric complexes **2** were converted into the triphenylphosphine monomers **3** by reaction with triphenylphosphine (Table 1). In the IR spectra of these monomers the >C=N group absorbed in the range 1598–1628 cm^{-1}, compared with about 1630 cm^{-1} in the free ligands **1**. In the ^1H NMR spectrum, the imine hydrogen absorption undergoes an upfield shift of ca. 1.9 ppm, compared with the parent imines (Table 2). Additionally, H(5) is shifted from about 7.0 to about 6.0 ppm; both resonances are split by coupling to ^{31}P. In the ^{13}C NMR spectra of the monomeric complexes (Table 3), the imine carbon resonates at about 170 ppm, with a small $^{13}C-^{31}P$ coupling evident (3–4 Hz). The C(3) resonance at about 149 ppm, and the C(4) absorption at about 121 ppm exhibit $^{13}C-^{31}P$ couplings of about 6 and 12 Hz, respectively. Assignments for all of the carbon atoms have been made.

We have found that if the *N*-phenylbenzaliminetriphenylphosphine complexes **3b**, **3h**, **3j** and **3l** are treated with an excess of triphenylphosphine, the chelate ring is opened to yield the (presumably) *trans*-bis(triphenylphosphine)palladium(II) complexes of type **4**. The complex **4l** has been described before [18]. The chemical shift values in the ^1H and ^{13}C NMR spectra for C_5-H, >C(H)–N= and $-C^*=N-$ groups are, as expected, very similar to the values found in the uncomplexed benzalimines. These bis(triphenylphosphine) complexes were found to dissociate in solution, as indicated by low molecular weight determinations in solution and by broadened NMR absorptions.

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