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Polychlorophenyl Nickel(II) Complexes with Triethylphosphine

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A series of neutral, square planar compounds of nickel and triethylphosphine containing different polychlorophenyl groups, of the type $[NiXR(PEt_3)_2]$ *with* $R = C_6Cl_5$, *2,3,4,5- 2,3,4,6- and 2,3,5,6-*C_6Cl_4H, *2,4,6- and 2,3,6-*$C_6Cl_3H_2$ *have been prepared. Compounds with* $X = Cl$ *were made by action of Grignard reagents on* $[NiCl_2(PEt_3)_2]$, *a process which in some cases occur via metalation. The other compounds of the series were made by metathetical reactions, for* $R = C_6Cl_5$, $X = Br, NCS, NCO, N_3, NO_2, CN, OC_6Cl_5$; *for* $R = 2,3,5,6\text{-}C_6Cl_4H$ *or* $2,3,6\text{-}C_6Cl_3H_2$, $X = NCS$ *and* NO_2. *Compounds of the type* $[NiRL(PEt_3)_2]\ ClO_4$, $R = C_6Cl_5$, $L = C_3H_4N_2$, *py,* α *and* β*-pic;* $R = 2,3,5,6\text{-}C_6Cl_4H$, $L = \gamma$*-pic, and* $[Ni(C_6Cl_5)(\gamma\text{-pic})_2(PEt_3)]ClO_4$ *have also been prepared. Action of gaseous HCl cleaves the metal–carbon bond in all compounds excepting that containing the pentachlorophenyl group.*

Introduction

The stability of σ(M–C) bonds in nickel organometallic compounds with alkyl or aryl groups described indicates a strong dependence on steric factors, namely the presence of bulky substituents of the organic group in *ortho* position to the M–C bond [1] and the volume of the phosphine ligand [2]. On the other hand, a greater stability has been observed depending on the electronegativity of the organic group: the compounds with polychlorophenyl ligands are more stable the larger the number of chlorine atoms on the aromatic ring [3].

In order to estimate the importance of the size of the phosphine ligand, a series of compounds containing PEt_3, analogous to those described previously with PPh_3 and dpe [4], have been prepared. PEt_3 may be considered smaller than PPh_3 according to Tolman's cone angle scale (132° for PEt_3 and 145° for PPh_3) [2]. Furthermore, PEt_3 does not have the additional stability due to the chelate effect which dpe (125° cone angle) does have.

Results and Discussion

Preparation

The neutral compounds $[NiClR(PEt_3)_2]$ have been made by action of the corresponding polychlorophenyl Grignard reagents on $[NiCl_2(PEt_3)_2]$. The Grignard reagents can be made by either insertion of Mg in the C–Cl bond

$$C_6H_{6-n}Cl_n + Mg \rightarrow C_6H_{6-n}Cl_{n-1}MgCl \qquad \text{(I)}$$

metalation process of the polychlorobenzene excess

$$C_6H_{6-n}Cl_{n-1}MgCl + C_6H_{6-n}Cl_n \rightarrow C_6H_{5-n}Cl_nMgCl + C_6H_{6-n+1}Cl_{n-1} \qquad \text{(II)}$$

or metalation with benzylmagnesium chloride

$$C_6H_{6-n}Cl_n + C_6H_5CH_2MgCl \rightarrow C_6H_{5-n}Cl_nMgCl + C_6H_5CH_3 \qquad \text{(III)}$$

Grignard reagents which lead to $[NiCl(C_6Cl_5)(PEt_3)_2]$* and $[NiCl(2,3,6\text{-}C_6H_2Cl_3)(PEt_3)_2]$ are prepared according to reaction (I); those which lead to $[NiCl(2,3,4,6\text{-}C_6Cl_4H)(PEt_3)_2]$, $[NiCl(2,3,5,6\text{-}C_6Cl_4H)(PEt_3)_2]$, and $[NiCl(2,4,6\text{-}C_6Cl_3H_2)(PEt_3)_2]$ are prepared according to reaction (II); and that leading to $[NiCl(2,3,4,5\text{-}C_6Cl_4H)(PEt_3)_2]$ is prepared according to reaction (III).

It has not been possible to prepare other trichlorophenyl derivatives with only one chlorine in *ortho* position using Grignard reagents. However such derivatives can be made by oxidative addition of polychlorobenzene groups on Ni(0) compounds. Thus, addition of $1,2,4,5\text{-}C_6H_2Cl_4$ to $[Ni(PPh_3)_4]$ leads to $[NiCl(2,4,5\text{-}C_6H_2Cl_3)(PPh_3)_2]$ [5] and analogously from $1,2,4\text{-}C_6H_3Cl_3$ and $[Ni(C_2H_4)(PEt_3)_2]$, $[NiCl(2,5\text{-}C_6H_3Cl_2)(PEt_3)_2]$ can be prepared [6].

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*This compound and $[NiI(C_6Cl_5)(PEt_3)_2]$ have been previously reported [1].

TABLE I. Analytical Data [Found (Calcd.)%] and Melting Points (°C).

Compound	Analysis				M.p. °C
	C	H	Total Halogen	N	
$[NiBr(C_6Cl_5)(PEt_3)_2]$	35.0	4.9	40.8		150–2
	(34.6)	(4.8)	(41.2)		
$[NiNCS(C_6Cl_5)(PEt_3)_2]$	37.6	5.0	29.5	2.2	205–7
	(37.9)	(5.0)	(29.4)	(2.3)	
$[NiNCO(C_6Cl_5)(PEt_3)_2]$	39.1	5.2	30.4	2.3	199–201
	(38.9)	(5.1)	(30.2)	(2.4)	
$[NiN_3(C_6Cl_5)(PEt_3)_2]$	36.9	5.2	30.4	7.0	156–8
	(36.9)	(5.1)	(30.2)	(7.2)	
$[NiNO_2(C_6Cl_5)(PEt_3)_2]$	36.8	5.2	29.8	2.1	167–9
	(36.6)	(5.1)	(30.0)	(2.4)	
$[NiCN(C_6Cl_5)(PEt_3)_2]$	39.8	5.2	31.5	2.6	154–6
	(40.0)	(5.3)	(31.0)	(2.5)	
$[NiOC_6Cl_5(C_6Cl_5)(PEt_3)_2]$	35.6	3.9	44.1		125 dec.
	(35.6)	(3.7)	(43.8)		
$[NiCl(2,3,4,5\text{-}C_6Cl_4H)(PEt_3)_2]$	39.1	5.8	32.0		122–5
	(39.6)	(5.7)	(32.5)		
$[NiCl(2,3,4,6\text{-}C_6Cl_4H)(PEt_3)_2]$	39.1	5.7	31.9		138–40
	(39.6)	(5.7)	(32.5)		
$[NiCl(2,3,5,6\text{-}C_6Cl_4H)(PEt_3)_2]$	38.5	5.7	31.9		144–5
	(39.6)	(5.7)	(32.5)		
$[NiNCS(2,3,5,6\text{-}C_6Cl_4H)(PEt_3)_2]$	40.5	5.7	24.0	2.4	153–4
	(40.2)	(5.5)	(25.0)	(2.5)	
$[NiNO_2(2,3,5,6\text{-}C_6Cl_4H)(PEt_3)_2]$	39.0	5.6	26.1	2.0	124–5
	(38.9)	(5.6)	(25.5)	(2.5)	
$[NiCl(2,4,6\text{-}C_6Cl_3H_2)(PEt_3)_2]$	42.5	6.5	27.6		160–3
	(42.3)	(6.3)	(27.7)		
$[NiCl(2,3,6\text{-}C_6Cl_3H_2)(PEt_3)_2]$	43.4	6.4	27.5		123–4
	(42.3)	(6.3)	(27.7)		
$[NiNCS(2,3,6\text{-}C_6Cl_3H_2)(PEt_3)_2]$	43.0	6.0	20.5	2.7	179–80
	(42.8)	(6.0)	(19.9)	(2.6)	
$[NiNO_2(2,3,6\text{-}C_6Cl_3H_2)(PEt_3)_2]$	42.1	6.1	21.5	2.4	115–6
	(41.5)	(6.2)	(20.4)	(2.7)	
$[NiNCS(C_6Cl_5)(\gamma\text{-pic})(PEt_3)]$	39.8	4.1	30.7	4.9	142 dec.
	(39.5)	(3.8)	(30.7)	(4.8)	
$[Ni(C_6Cl_5)/C_3H_4N_2)(PEt_3)_2]ClO_4$	34.8	4.8	29.7	8.2	181–3
	(35.4)	(4.8)	(29.9)	(8.2)	
$[Ni(C_6Cl_5)(py)(PEt_3)_2]ClO_4$	38.1	5.0	29.7	1.6	185–8
	(38.2)	(4.9)	(29.4)	(1.9)	
$[Ni(C_6Cl_5)(\alpha\text{-pic})(PEt_3)_2]ClO_4$	38.8	5.0	28.9	2.0	167–70
	(39.1)	(5.0)	(28.9)	(1.9)	
$[Ni(C_6Cl_5)(\beta\text{-pic})(PEt_3)_2]ClO_4$	39.1	5.0	28.6	1.9	191–3
	(39.1)	(5.0)	(28.9)	(1.9)	
$[Ni(C_6Cl_5)(\gamma\text{-pic})_2(PEt_3)]ClO_4$	40.5	4.1	30.1	4.0	195–7
	(40.5)	(4.1)	(29.9)	(3.9)	
$[Ni(2,3,5,6\text{-}C_6Cl_4H)(\gamma\text{-pic})(PEt_3)_2]ClO_4$	41.2	5.5	25.5	2.0	188–92
	(41.0)	(5.5)	(25.3)	(2.0)	

The impossibility of preparing organometallic compounds of the type $[NiR_2L_2]$ using this method may be attributed to kinetic factors arising from the square planar geometry of $[NiClRL_2]$ [7, 8]. Recently, P. Royo [9] has prepared $[Ni(C_6Cl_5)_2dpe]$ by reacting $[Ni(CO)_2dpe]$ with $ClTl(C_6Cl_5)_2$.

Replacement of the Cl ligand was attempted in some cases in order to prepare analogous series to those already prepared: $[MX(C_6Cl_5)(PEt_3)_2]$ (M = Pd, Pt) and $[NiX(C_6Cl_5)P_2]$ (P = PPh_3 or P_2 = dpe [4, 10, 11]. The reactions may be carried out by reacting alkali metal or silver salts with the organometallic compound under reflux in acetone solution. In this faction, the following products have been prepared: $[NiX(C_6Cl_5)(PEt_3)_2]$ with X = Br, I, NCS, NCO, N_3, NO_2, CN, OC_6Cl_5, and [NiXR-

TABLE II. PMR Signals of the Nitrogen-containing Ligands (δ).

$[Ni(C_6Cl_5)L_nP_{3-n}]ClO_4$	*ortho*	*meta–para*	CH_3 (L)
n = 1 L = py	9	7.98	
n = 1 L = αpic	9.12	7.75	3.45
n = 1 L = β-pic	8.7	7.78	2.50
n = 2 L = γ-pic	9.03[a]	7.17[d,b]	2.23[b]
		7.47[d,c]	2.36[c]
n = 1 L = imidazole	8.12 [2]	7.45 [4]	7.15 [5]

[a]Two superimposed doublets. [b]*Cis* with respect to C_6Cl_5. [c]*Trans* with respect to C_6Cl_5. [d]Doublet.

$(PEt_3)_2]$ with R = 2,3,6-$C_6Cl_3H_2$ and 2,3,5,6-C_6Cl_4H with X = NCS and NO_2, which were the only anions examined.

On reacting $AgClO_4$ with $[NiClR(PEt_3)_2]$ in acetone or benzene, AgCl separates out. It was not possible to isolate $[Ni(ClO_4)R(PEt_3)_2]$ in the solid state, however the analogous Pd derivative has been prepared [8]. The acetone solution show conductivities typical of 1:1 electrolytes [12] in agreement with a possible solvent coordination. The addition of potassium salts of the appropriate ligands results in formation of neutral compounds and precipitation of $KClO_4$. An excess of $AgClO_4$ does not lead to decomposition of the organometallic compounds and formation of silver complexes containing phosphines as is the case with dpe and PPh_3 [4]. Addition of bases like imidazole, α and β-picoline leads to ionic species of the type $[Ni(C_6Cl_5)L(PEt_3)_2]ClO_4$.

The only compound containing γ-pic with C_6Cl_5 which has been characterized is $[Ni(C_6Cl_5)(\gamma\text{-pic})_2(PEt_3)]ClO_4$, but $[Ni(2,3,5,6\text{-}C_6Cl_4H)(\gamma\text{-pic})(PEt_3)_2]ClO_4$ is obtained from benzene solutions of $[NiClO_4(2,3,5,6\text{-}C_6HCl_4)(PEt_3)_2]$. Attempts to prepare salts with anions other than perchlorate lead to the following process

$$[NiRL(PEt_3)_2]ClO_4 + KX \rightarrow KClO_4 + L + [NiXR(PEt_3)_2]$$

however, $[NiNCS(C_6Cl_5)(\gamma\text{-pic})(PEt_3)]$ is obtained from $[Ni(C_6Cl_5)(\gamma\text{-pic})_2(PEt_3)]ClO_4$ and KNCS. Attempts to replace the phosphine ligands by the heterocyclic base were unsuccessful in contrast with Wada's report [13] on complexes of the type $[Ni(C_6Cl_5)(3,5\text{-lut})(P)_2]ClO_4$ (P = $PMePh_2$ and PMe_2Ph).

Characterization

All the compounds are stable as solids and in solution. Analytical and melting point data are given in Table I. Molar conductivities in acetone, at 18 °C, and concentration 10^{-4} *M* are 1–3 ohm^{-1} cm^2 mol^{-1} for the neutral compounds and 145–155 ohm^{-1} cm^2 mol^{-1} for the ionic compounds. All the substances prepared have a square-planar geometry as shown by its diamagnetic character. PMR spectra of the compounds containing Br^-, I^- and CN^- show the signal of the methyl groups of triethylphosphine as a pseudoquintuplet which agrees with a *trans* geometry, similarly to that observed in other nickel, palladium and platinum complexes [14, 15]. In all other cases, methyl and methylene signals are totally or partially superimposed. The signals of the protons of coordinated polychlorophenyl are observed at:

R:	2,3,5,6-C_6HCl_4	2,3,4,5-C_6HCl_4	2,3,4,6-C_6HCl_4	2,4,6-$C_6H_2Cl_3$	2,3,6-$C_6H_2Cl_3$
δ(ppm):	7.2	7.3	7.1	6.95	6.9

The proton signals of the nitrogen-containing ligands in the ionic compounds are given in Table II. The organometallic cation $[Ni(C_6Cl_5)(\gamma\text{-pic})_2PEt_3]ClO_4$ has a *cis* geometry as shown by the duplicity of infrared bands of ν_{11} of γ-picoline [16], and by the duplicity of PMR methyl signals of γ-picoline.

The signal of the α-picoline methyl group in the cationic complexes shows a marked shift towards lower fields with respect to its position in the free compound (δ = 2.55 ppm), a fact which according to Miller *et al.* [15], leads us to propose that α-picoline lies in a plane perpendicular to that of the complex.

The most important infrared bands due to the coordinated groups are given below: For PEt_3, bands appear at 2970–2860, 1450, 1405, 1030, 800–700 cm^{-1} [17]; the intensity and position of the PEt_3 bands in the 700–800 cm^{-1} zone show a marked dependence on the other ligands of the complex (X and R). This fact is probably due to the different conformations which PEt_3 may adopt. For the polychlorophenyl groups bands are observed at: 1315–1325 and 1310–1315, 1285–1280, 1220, 665–670, and 605–610 cm^{-1} for C_6Cl_5; 1380, 1310, 790 and 630 for 2,3,4,5-C_6Cl_4H; 1380, 1300, 790 and 630 cm^{-1} for 2,3,4,6-C_6HCl_4; 1355, 1300, 1150, 840 and 650 cm^{-1} for 2,3,5,6-C_6HCl_4; 1400, 1320, 1250, 1150, 800 and 735 cm^{-1} for 2,3,6-$C_6H_2Cl_3$ [3, 18]. The bands which appear practically in all cases in the lower region of the spectrum, at 360 and 310 cm^{-1}, may be assigned to Ni–Cl vibrations.

Reactivity

Chlorine

The action of gaseous chlorine on $CHCl_3$ solutions of the compounds of the type $[NiX(C_6Cl_nH_{5-n})(PEt_3)_2]$ was examined. Cleavage of the Ni–C bond occurs in all cases along with formation of Ni^{2+} and $C_6Cl_{n+1}H_{5-n}$, similarly to that observed in compounds containing dpe and PPh_3. Addition of the stoichiometric quantity of chlorine dissolved in CCl_4 leads to the same results.

Hydrogen chloride

The action of gaseous HCl on chloroform solutions of the compounds studied results in cleavage of the Ni–C bond in all cases excepting those containing C_6Cl_5. The analogous PPh_3 compounds resist the action of HCl when the tri and tetrachlorophenyl groups contain two *ortho* chlorine atoms. On the contrary, $[NiCl(2,3,4,5\text{-}C_6Cl_4H)(PPh_3)_2]$ (with only one ortho chlorine atom) is decomposed by the same reagent. This different behaviour may be due to the smaller size of PEt_3 (according to the scale of cone angle) as compared to PPh_3. These facts show the importance of the steric factor for nickel compounds in both the aryl group which must have bulky *ortho* substituents and the size of the phosphine group.

The X group is replaced by Cl in the compounds of the type $[NiX(C_6Cl_5)(PEt_3)_2]$ excepting the cases when X = Br, I, NCS, and CN, in which cases the compounds remain unchanged. It is noteworthy that for the analogous series of palladium compounds [11] replacement of X by Cl is attained in all cases. Passage of HCl on the ionic compounds of the type $[NiRL(PEt_3)_2]ClO_4$ leads to $[NiClR(PEt_3)_2]$ which reacts as the corresponding neutral substance.

Phosphine exchange

Replacement of PEt_3 by PPh_3 was examined in the compounds prepared but the starting material was recovered unchanged. The inverse reaction (treatment of the PPh_3 complexes with PEt_3 under reflux in $CHCl_3$ for 3 hours) leads to the PEt_3 derivatives. The behaviour agrees with Nakamura and coworkers [19] who suggest that the replacement of a bulky by a smaller phosphine is the favourable process.

Experimental

$[NiClR(PEt_3)_2]$

Reactions were carried out under N_2, from $[NiCl_2(PEt_3)_2]$ which was obtained by Jensen's method [20].

$R = 2,3,6\text{-}C_6H_2Cl_3$ or C_6Cl_5

The Grignard reagent was prepared from $1,2,3,4\text{-}C_6H_2Cl_4$ or C_6Cl_6 (20 mmol) and Mg (25 mmol) in THF (15 ml) using C_2H_5MgBr as initiator. The mixture was maintained 30 min under reflux and after cooling it was added onto 1.5 g of $[NiCl_2(PEt_3)_2]$. The product which precipitated from the brown solution on cooling to –10 °C, was washed with water and recrystallized from dichloromethane/methanol. The yield is about 30% and 80% respectively.

$R = 2,3,4,6\text{-}C_6HCl_4$; $2,3,5,6\text{-}C_6HCl_4$; $2,4,6\text{-}C_6H_2Cl_3$

The Grignard reagent was prepared by reacting 20 mmol of either $1,2,3,5\text{-}C_6H_2Cl_4$, $1,2,4,5\text{-}C_6H_2Cl_4$ or $1,3,5\text{-}C_6H_3Cl_3$ with magnesium (25 mmol) in THF (15 ml) using C_2H_5MgBr as initiator. The mixture was refluxed for 4–5 hr (for the tetrachlorobenzene derivatives) and for 2–3 hr (for the trichlorobenzene derivative). After allowing to cool to room temperature $[NiCl_2(PEt_3)_2]$ (1 g) was added and the substances which separated at –10 °C were washed with water and recrystallized from dichloromethane/methanol. The yield was about 60%.

$R = 2,3,4,5\text{-}C_6HCl_4$

$C_6H_5CH_2MgCl$ was prepared from Mg (25 mmol) and benzyl chloride (20 mmol) in THF (20 ml) stirring constantly for ½ hr. The solution was added to $1,2,3,4\text{-}C_6Cl_4H_2$ (16 mmol) and the mixture was refluxed for ½ hr. After cooling, the reagent was added to $[NiCl_2(PEt_3)_2]$ (1 g). The rest of the procedure is the same as above. The yield was about 50%.

$[NiXR(PEt_3)_2]$, $X = Br^-, NCS^-, NCO^-, NO_2^-, N_3^-$

By action of alkali metal salts

Replacement of Cl in the compounds $[NiClR(PEt_3)_2]$ was attained by refluxing them with an excess of the potassium salts of the ligands NCS^-, NCO^-, NO_2^- or NaN_3 or LiBr in acetone for 2–5 hr. The resulting solution was evaporated to dryness, the residue washed with water and recrystallized from dichloromethane/ethanol. Yields were about 80–90%. Infrared bands (cm^{-1}) NCS: 2090 ν_3; 842 ν_1; 340–260 $\nu_{(Ni\text{–}N)}$ NCO: 1330 ν_1; 590, 600 ν_2; 2230 ν_3; 400 $\nu_{(Ni\text{–}N)}$, N_3: 2070 ν_3; 1340 ν_1; 400 $\nu_{(Ni\text{–}N)}$. NO_2: 1350–1370 ν_3; 1320 ν_1; 810 ν_2; 545 ρ_w; 340–360 $\nu_{(Ni\text{–}N)}$.

$[NiX(C_6Cl_5)(PEt_3)_2]$, $X = CN^-, OC_6Cl_5^-$

Using silver salts

Acetone solutions of $[NiCl(C_6Cl_5)(PEt_3)_2]$ were treated with the stoichiometric amount of AgCN or $AgOC_6Cl_5$ in the cold for ½ or 6 hr respectively after which the AgCl precipitated was filtered off. The resulting solution was evaporated to dryness. The residue was recrystallized from dichloromethane/methanol. Yields were about 40%. Infrared bands (cm^{-1}) CN: 2110 $\nu_{(CN)}$ and 450 $\nu_{(Ni-C)}$. OC_6Cl_5: 1540, 1490, 1450, 1360, 1220, 1000, 780, 650, and 535.

[NiRL(PEt$_3$)$_2$]ClO$_4$

Silver perchlorate (1 mmol) was added to [NiClR-$(PEt_3)_2$] (1 mmol) in benzene (20 ml) at room temperature and the mixture was stirred for 5 min. After filtering the AgCl formed, excess of the organic base was added and the mixture was stirred for a period of time between 15 min and 2 hr depending on the base. The desired ionic products were precipitated on cooling to 5 °C. Infrared bands: imidazole: 3320, 3160, 3130, 1535, 1498, and 850. Pyridine: 1600, 1205, 1015 and 710 cm^{-1}. α-pic: 1610, 1565, 1490, 805, 760 and 480. β-pic: 1610, 1580, 1480, 790, 710 and 495. γ-pic, see below.

[Ni(C$_6$Cl$_5$)(γ-pic)$_2$(PEt$_3$)]ClO$_4$

An excess of γ-picoline was added to a solution of $[NiClO_4(C_6Cl_5)(PEt_3)_2]$ prepared as above and the resulting solution was stirred at 40 °C for ½ hr. On cooling to 0 °C, the desired ionic product was precipitated. Infrared bands: γ-picoline: 1620, 1505, 1425, 1210, 830, 810, 550, 510, and 495 cm^{-1}.

[NiNCS(C$_6$Cl$_5$)(γ-pic)(PEt$_3$)]

KNCS (0.5 g) was added to a solution of $[Ni(C_6Cl_5)(\gamma\text{-pic})_2(PEt_3)]ClO_4$ (1 mmol) in 20 ml of acetone and the mixture was stirred at room temperature for 2 hr. The solution was concentrated to 5 ml and cooled to –5 °C. The precipitate was collected, washed with water and recrystallized from dichloromethane/methanol. Infrared bands: γ-picoline: 1620, 1500, 1420, 1210, 805, 550 and 495 cm^{-1}.

Analyses

C, H and N determinations were carried out at the Institute of Applied Organic Chemistry of Catalunya. Halogens were determined by Schöniger's method.

Spectra

Infrared spectra were recorded on a Beckman IR 20A spectrophotometer and samples were prepared as KBr disks or Nujol mulls. PMR spectra were recorded on a Perkin Elmer R-12A using CCl_4 or $CDCl_3$ as solvents and TMS as reference.

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