PENTAFLUOROPHENYL DERIVATIVES OF TRANSITION METALS

II*. BIS(CYCLOPENTADIENYL)BIS(PENTAFLUOROPHENYL)TITANIUM AND RELATED COMPOUNDS

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In recent years numerous compounds have been synthesized in which perfluoroalkyl or other highly fluorinated alkyl groups are bonded to metals[2,3]. Isolation of these compounds suggested the possible existence of related substances involving other fluorocarbon systems, notably the pentafluorophenyl group. With the discovery of pentafluorophenyl derivatives of boron[4], tin[5,6,7], and some of the transition metals[1] this area of chemistry is now developing rapidly, a natural consequence of the earlier preparation of pentafluorophenylmagnesium iodide and bromide[8], pentafluorophenyllithium[9], and the general availability of pentafluorophenyl bromide.

Current interest in factors responsible for stabilizing transition metal to carbon σ bonds makes a study of the pentafluorophenyl derivatives of the transition metals desirable. Herein, we describe certain pentafluorophenyl complexes of titanium.

Of the known compounds having titanium–carbon σ bonds the cyclopentadienyl aryl derivatives $(\pi\text{-}C_5H_5)_2Ti(Ar)_2$ are the most stable, and have thus been the best characterised[10]. Hence, in order to make useful comparisons between hydrocarbon complexes on the one hand and fluorocarbon complexes on the other the preparation of bis(π-cyclopentadienyl)bis(σ-pentafluorophenyl)titanium was attempted. Treatment of bis(π-cyclopentadienyl)titanium dichloride suspended in diethyl ether with a solution of pentafluorophenyllithium in ether, in a 1:2 molar ratio, affords $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ in good yield. Also formed during this reaction is a small quantity of the chloride $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$. The proportion of the latter compound is readily increased by mixing the reactants in a 1:1 ratio.

The two compounds $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ and $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$ are orange crystalline solids soluble in benzene, ether and other organic solvents. They are stable in air over periods of several months, and do not decompose appreciably below their melting points, which are over 200° C. Prolonged pyrolysis of bis(π-cyclopentadienyl)bis(σ-pentafluorophenyl)titanium *in vacuo* at 150° C results in partial decomposition to give the fluoride $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)F$. The latter is clearly formed by fluorine migration from a pentafluorophenyl group to the metal, a mode of decomposition characteristic of other fluorocarbon–metal compounds[2]. It is evident from the fore-

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going properties that the new pentafluorophenyltitanium complexes are more chemically robust than their aryl analogues $(\pi\text{-}C_5H_5)_2Ti(Ar)_2$, in that bis($\pi$-cyclopentadienyl)bis($\sigma$-phenyl)titanium decomposes[10] slowly at room temperature, and rapidly above 100°.

During preparation of the pentafluorophenyltitanium compounds by treating bis(π-cyclopentadienyl)titanium dichloride with pentafluorophenyllithium, simultaneous formation of milligram quantities of a pale yellow solid was observed. The infrared spectrum of this compound showed that it contained pentafluorophenyl groups, while a band in the spectrum at 3625 cm^{-1} was indicative of the presence of an hydroxyl group. By analysis the compound was characterized as $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)OH$. It was subsequently prepared directly by the base hydrolysis of a sample of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$. Formation of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)OH$ on addition of pentafluorophenyllithium to bis(π-cyclopentadienyl)titanium dichloride presumably occurred due to the ether used to suspend the $(\pi\text{-}C_5H_5)_2TiCl_2$ being incompletely dried. Consequently, on addition of pentafluorophenyllithium partial hydrolysis afforded lithium hydroxide, which reacted with the $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$ present to give $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)OH$. In agreement with this an experiment using diethyl ether which had been deliberately only partially dried gave substantial amounts of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)OH$.

Hydrolysis of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$ with consequent replacement of chloride by hydroxide whilst leaving the $\sigma\text{-}C_6F_5Ti$ grouping intact, is of considerable interest, as also is our observation that $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ withstands prolonged heating at 100° C with 20 % aqueous sodium hydroxide. It has been observed previously[11] that fluorine atoms of fluoroalkyl groups attached to manganese or iron are labile. Thus treatment of the polyfluoroalkylmanganese and -iron compounds with aqueous base affords fluoride ion, in marked contrast to the behaviour of the pentafluorophenyltitanium compounds.

The observation[11] that polyfluoroalkylmanganese and iron compounds react at elevated temperatures with hydrogen chloride gas in Pyrex vessels to give silicon tetrafluoride is further evidence of the lability of the fluorine atoms in these complexes. A study of the effect of hydrogen chloride on the pentafluorophenyltitanium compounds showed a completely different mode of behaviour. Treatment of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ or $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$ with an excess of hydrogen chloride gas at 150° C, results in essentially quantitative cleavage of the pentafluorophenyl groups to produce pentafluorobenzene. Bis(π-cyclopentadienyl)titanium dichloride is also formed in these reactions. Treatment of bis(π-cyclopentadienyl)bis(pentafluorophenyl)titanium with excess aqueous hydrochloric acid in tetrahydrofuran also results in formation of bis(π-cyclopentadienyl)titanium dichloride. If a deficiency of aqueous acid is used, then $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ affords a mixture of $(\pi\text{-}C_5H_5)_2TiCl_2$ and $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$. In contrast, however, to the ready formation of bis(π-cyclopentadienyl)titanium dichloride from $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$, treatment of the latter with an excess of hydrofluoric acid yields only $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)F$.

Bis(π-cyclopentadienyl)titanium dichloride is also formed when $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ is heated with titanium(IV) chloride in diethyl ether or with dimethyltin dichloride in tetrahydrofuran solution.

It has been reported[5] that whereas pentafluorophenyltin compounds are stable in aqueous ethanol, addition of catalytic amounts of halide ion leads to rapid hydrolysis producing pentafluorobenzene. Such behaviour was not observed with

$(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$, which was unaffected after being refluxed for several hours in a methanol solution containing chloride ion.

During studies on the pentafluorophenyltitanium compounds a rapid reaction was observed between $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$ and sodium ethoxide, affording the new compound $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)OC_2H_5$. Similar reactions yielding other complexes $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)R$ derived from $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$ are under study.

Infrared spectral bands of several of the pentafluorophenyltitanium compounds are listed in the EXPERIMENTAL section. From this study we conclude that bands characteristic of the pentafluorophenyl group occur near 1065(s), 1050(m), 960(vs) and 930(w) cm^{-1}.

EXPERIMENTAL

Microanalytical determinations were made at the Alfred Bernhardt Mikroanalytisches Laboratorium im Max-Planck-Institut für Kohlenforschung, Mulheim (Ruhr). Pentafluorophenyl bromide was obtained from Imperial Smelting Co., Avonmouth, Bristol, England, and bis(π-cyclopentadienyl)titanium dichloride from Arapahoe Chemicals Inc., Boulder, Colorado, U.S.A.

Bis(π-cyclopentadienyl)bis(pentafluorophenyl)titanium and bis(π-cyclopentadienyl)-pentafluorophenyltitanium chloride

Pentafluorophenyllithium [obtained[9] from C_6F_5Br (10.0 g, 40.5 mmoles) and a 15 % hexane solution of $n\text{-}C_4H_9Li$ (17.3 g, 40.5 mmoles)] in diethyl ether at −78° under nitrogen was added dropwise over 10 min to a stirred suspension of bis(cyclopentadienyl)titanium dichloride (5.0 g, 20.1 mmoles) in 750 ml of dry diethyl ether at room temperature under nitrogen. Lithium chloride precipitated and the solution became orange. The mixture was stirred for 16 h, filtered, and the ether distilled from the filtrate leaving 8.5 g of an orange solid residue. A benzene solution of this solid was chromatographed on Florisil, and the two orange bands which developed were eluted with benzene. The first eluate, containing the majority of the material, was collected, evaporated to dryness and the solid recrystallised from a diethyl ether–hexane mixture to give orange needles (4.5 g, 44 % yield) of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ [Found: C, 51.8; H, 2.2; F, 36.9; Ti, 9.2; mol.wt. (vapour pressure osmometer), 521. $C_{22}H_{10}F_{10}Ti$ calcd.: C, 51.6; H, 2.0; F, 37.1; Ti, 9.4 %; mol.wt. 512.], m.p. 228–230° C.

From the second eluate 30 mg of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$ was obtained as a pale orange solid. Treatment of bis(π-cyclopentadienyl)titanium dichloride with pentafluorophenyllithium in a 1:1 ratio gave the mono(pentafluorophenyl)titanium compound in larger quantity. In a typical experiment bis(π-cyclopentadienyl)titanium dichloride (5.0 g, 20.1 mmoles) and pentafluorophenyllithium [prepared from C_6F_5Br (5.0 g, 20.25 mmoles) and 8.65 g of 15.1 % $n\text{-}C_4H_9Li$ in hexane (20.25 mmoles)] were stirred together in diethyl ether. Subsequent work up of benzene soluble material by chromatography afforded 2.2 g, (29 % yield based on pentafluorophenyllithium used in the reaction) of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$ [Found: C, 50.7; H, 2.7; F, 24.9; Ti, 12.5; Cl, 8.9; mol.wt. (vapour pressure osmometer) 380. $C_{16}H_{10}F_5ClTi$ calcd.: C, 50.5; H, 2.6; F, 25.0; Ti, 12.6; Cl, 9.2 %; mol.wt. 380], m.p. 201–3° C, and 1.3 g, (25 % yield) of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$. Some $(\pi\text{-}C_5H_5)_2TiCl_2$ (2.6 g), which is benzene-insoluble was recovered, thereby accounting for 93 % of the bis(π-cyclopentadienyl)titanium dichloride taken for reaction.

The compound $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)OH$

When the benzene-soluble material from reactions between pentafluorophenyllithium and bis(π-cyclopentadienyl)titanium dichloride was chromatographed the two orange bands on the Florisil column were followed by a much smaller yellow band which was finally eluted using a 50 % mixture of benzene and diethyl ether. Evaporation of solvent followed by recrystallization from a diethyl ether–hexane mixture afforded bright yellow crystals, m.p. 183–185° C (with decomposition). The crystals collected from several experiments were analysed. [Found: C, 52.8; H, 3.1; Ti, 13.2; F, 25.8; mol.wt. 353. $C_{16}H_{11}F_5OTi$ calcd.: C, 53.0; H, 3.0; Ti, 13.3; F, 26.2 %; mol.wt. 362.] The yellow complex $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)OH$ is soluble in common organic solvents. We have referred previously to the band in the infrared spectrum in the O–H stretching region. A list of all the significant infrared spectral bands is given in a later section, as is the preparation of the compound directly from $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$.

Pyrolysis of bis(π-cyclopentadienyl)bis(σ-pentafluorophenyl)titanium

A 100 ml Pyrex reaction bulb was charged with 497 mg (0.971 mmoles) of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$. The vessel was attached to the vacuum line, evacuated and sealed. After heating at 110° C for 2 days no reaction was observed. The temperature was then raised to 150° C, and heating continued for 24 h. Formation of yellow crystals and a brown solid was observed. On opening the reaction vessel to the vacuum system a barely detectable amount of gas condensable at —78° C was obtained. Solid remaining in the bulb was treated with diethyl ether. After filtration, the resulting solution was evaporated to dryness and the residue chromatographed in the usual way. The only product present in significant quantity appeared as a yellow band eluting with 50 % diethyl ether–petroleum ether. After evaporation of solvent the yellow residue was sublimed at 140° (10^{-3} mm) to give 30 mg (8.5 % yield) of yellow crystalline $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)F$ [Found: C, 53.2; H, 3.0; F, 30.7; Ti, 12.7; mol.wt. 391. $C_{16}H_{10}F_6Ti$ calcd.: C, 52.8; H, 2.8; F, 31.0; Ti, 13.2 %; mol.wt. 364.], which decomposes without melting at 240° C.

Reactions between the pentafluorophenyltitanium compounds and aqueous base

(*a*) *Bis(π-cyclopentadienyl)bis(pentafluorophenyl)titanium.* A 357 mg (0.7 mmole) sample of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ and 3 ml of 20 % aqueous sodium hydroxide were sealed together in an evacuated 250 ml Pyrex bulb and heated at 100° C for 8 days. After this time no reaction was apparent, and the orange starting material appeared not to have been wetted by the aqueous solution. The bulb was opened to the vacuum system, but no volatile product other than water was recovered. The solid present was washed with water and then recrystallised to give 212 mg (60 % recovery) of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$, identified by its melting point. Some product was lost in work-up, accounting very probably for the less than complete recovery of starting material. The aqueous solution recovered was acidified to pH 5 with acetic acid and calcium chloride added, but no calcium fluoride was observed to precipitate.

(*b*) *Bis(π-cyclopentadienyl)pentafluorophenyltitanium chloride.* A 400 mg (1.05 mmoles) sample of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$ was added to a mixture of 5 ml of water and 25 ml of tetrahydrofuran. After refluxing for ½ h no colour change from orange to yellow occurred, so a small pellet of potassium hydroxide was added. With continued refluxing, the mixture turned yellow. After 6 h the mixture was filtered. Solvent was removed from the filtrate affording a yellow residue. This was dissolved in benzene and chromatographed. A yellow band was eluted with 50% ether–benzene mixture to give 160 mg (44% yield) of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)OH$. The identity of the hydroxide was confirmed by comparing its infrared spectrum and m.p. with that of the previously analysed $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)OH$ (see above).

Reactions between the pentafluorophenyltitanium compounds and hydrogen chloride

(*a*) *Experiments using hydrogen chloride gas.* A 402 mg (0.785 mmole) sample of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ was weighed into a 250 ml Pyrex reaction bulb. The latter was attached to the vacuum system, evacuated, and then 5.0 mmoles of hydrogen chloride were condensed into the vessel. After sealing from the vacuum line, the bulb was heated at 110° C for 2 days, but no change was observed. The temperature was then raised to 150° C for 24 h, after which the bulb was attached to the vacuum system and opened. Fractionation of the volatile products led to the recovery of 3.5 mmoles of hydrogen chloride and isolation of 1.2 mmoles of pentafluorobenzene (identified by its infrared spectrum). The hydrogen chloride was returned to the bulb which was re-sealed and heated at 150° C for 4 days. This treatment led to a further uptake of 0.6 mmoles of hydrogen chloride and gave an additional 0.15 mmoles of pentafluorobenzene. The total amount of the latter recovered corresponded to 86% of the pentafluorophenyl groups in the original sample of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$. A portion of the solid residue in the bulb was recrystallised from toluene, and identified as $(\pi\text{-}C_5H_5)_2TiCl_2$ (45 mg) (identified by m.p. and mixed m.p.).

In an experiment similar to that just described, $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$ (190 mg, 0.500 mmoles) was heated with hydrogen chloride (6.25 mmoles) at 150° C for 6 days. This treatment afforded pentafluorobenzene (0.46 mmoles, 92% of theoretical), and unreacted hydrogen chloride (5.4 mmoles).

(*b*) *Experiments using aqueous hydrogen chloride.* A 512 mg (1 mmole) sample of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ was dissolved in 25 ml of tetrahydrofuran. Hydrochloric acid (1 ml, 12 mmoles) was added and the mixture was refluxed for 20 h. Removal of solvent afforded red crystals which were washed with ether, dried, and identified as $(\pi\text{-}C_5H_5)_2TiCl_2$ (211 mg, 85% yield) by m.p. and mixed m.p. There was no evidence for formation of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$. However, an experiment involving $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ (512 mg, 1 mmole) and a deficiency of aqueous hydrochloric acid (0.6 mmole), refluxed for 20 h in 25 ml of tetrahydrofuran, afforded after chromatography of the products $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$ (21 mg) and unreacted $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ (215 mg, 42% recovered). Bis(π-cyclopentadienyl)titanium dichloride was also produced.

Reaction between bis(π-cyclopentadienyl)bis(σ-pentafluorophenyl)titanium and hydrofluoric acid

A 512 mg (1 mmole) sample of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ was added to 25 ml of tetrahydrofuran containing 5 mmoles of hydrofluoric acid and 1 ml of water. The mixture was refluxed for 20 h. Solvent was removed giving an orange-yellow residue, which was dissolved in ether–benzene and chromatographed on a Florisil column. A yellow and an orange band developed. The latter, unreacted starting material, was eluted with benzene. The yellow band was eluted with a 20% ether–80% benzene mixture.

Recrystallisation from ether afforded $(\pi\text{-}C_5H_5)_2Ti(C_6H_5)F$. (Found: C, 52.9; H, 3.0; F, 30.8. $C_{16}H_{10}F_6Ti$ calcd.: C, 52.8; H, 2.8; F, 31.0%.) Yield 24%. The infrared spectrum of these yellow crystals was identical with that of the complex (see above) obtained by pyrolysis of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$.

Reaction between bis(π-cyclopentadienyl)pentafluorophenyltitanium chloride and sodium ethoxide

A 400 mg (1.05 mmoles) sample of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$ was refluxed under nitrogen with 25 ml (0.34 moles) of ethyl alcohol to which had been added 150 mg (6 mg-atom) of sodium. After 15 min reflux the colour of the solution had changed from orange to bright yellow. Removal of solvent afforded a yellow solid which was chromatographed. Elution with benzene, followed by recrystallisation from a diethyl ether–hexane mixture gave 155 mg (39% yield) of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)OC_2H_5$.(Found: C, 55.3; H, 3.8; F, 24.4; Ti, 12.1. $C_{18}H_{15}F_5OTi$ calcd.: C, 55.3; H, 3.8; F, 24.3; Ti, 12.3%.) M.p. 117° C. The ethoxide compound is stable in dry air and soluble in organic solvents.

Reaction between bis(π-cyclopentadienyl)bis(pentafluorophenyl)titanium and aqueous methanol

A 512 mg (1 mmole) sample of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ was refluxed (19 h) in 25 ml of methanol to which had been added water (1 ml) and chloride ion (2.5 mg NaCl). No colour change was observed and chromatography yielded only unreacted $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$.

Infrared spectra

These were recorded in carbon disulphide solution using a Perkin-Elmer model 237 Infracord Spectrophotometer.

$(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$: 2970(m), 2920(w), 2850(m), 1340(w), 1260(w), 1180(m), 1120(m), 1075(s), 1060(m), 1050 (w), 1030(w), 1020(w), 960(vs), 940(w), 840(s), 800(w).

$(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$: 2960(w), 2920(m), 1340(w), 1260(w), 1120(w), 1100(w), 1065(s), 1050(m), 1020(w), 960(vs), 930(w), 830(vs).

$(\pi\text{-}C_5H_5)_2Ti(C_6F_5)OH$: 3630(m), 2920(m), 1340(w), 1260(w), 1065(s), 1050(m, s), 1025(w), 960(vs), 930(vw), 820(vs).

$(\pi\text{-}C_5H_5)_2Ti(C_6F_5)OC_2H_5$: 2960(m), 2920(m), 2840(m), 1370(m), 1350 (w), 1335(m), 1265(m), 1250(m), 1135(s), 1115(vs), 1070(s), 1060(s), 1050(s), 1020(m), 950(vs), 925(m), 830(m), 810(vs).

$(\pi\text{-}C_5H_5)_2Ti(C_6F_5)F$: 2960(m), 2920(m), 2840(w), 1340(w), 1255(w), 1060(m), 1045(m), 1020(w), 950(vs), 815(s).

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SUMMARY

Treatment of bis(π-cyclopentadienyl)titanium dichloride with pentafluorophenyllithium affords a mixture of the new compounds $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ and $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$. Both of these complexes are significantly more robust than analogous aryltitanium compounds containing carbon–titanium σ-bonds. Pyrolysis of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ at 150° affords small quantities of $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)F$, which is best prepared by treating $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)_2$ with hydrofluoric acid. The pentafluorophenyl groups are cleaved as pentafluorobenzene by hydrogen chloride from the pentafluorophenyltitanium compounds. The compounds $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)OH$ and $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)OC_2H_5$ have been prepared from $(\pi\text{-}C_5H_5)_2Ti(C_6F_5)Cl$, by hydrolysis and alcoholysis respectively.

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