

# Metalate-Mediated Functionalization of P<sub>4</sub> by Trapping Anionic [Cp\*Fe(CO)<sub>2</sub>(η<sup>1</sup>-P<sub>4</sub>)]<sup>-</sup> with Lewis Acids

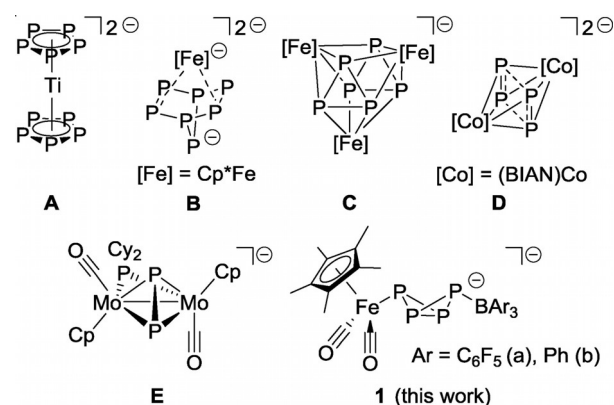
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The development of selective functionalization strategies of white phosphorus (P<sub>4</sub>) is important to avoid the current chlorinated intermediates. The use of transition metals (TMs) could lead to catalytic procedures, but these are severely hampered by the high reactivity and unpredictable nature of the tetrahedron. Herein, we report selective first steps by reacting P<sub>4</sub> with a metal anion [Cp\*Fe(CO)<sub>2</sub>]<sup>-</sup> (Cp\* = C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>), which, in the presence of bulky Lewis acids (LA; B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or BPh<sub>3</sub>), leads to unique TM-substituted LA-stabilized bicyclo[1.1.0]tetraphosphabutane anions [Cp\*Fe(CO)<sub>2</sub>(η<sup>1</sup>-P<sub>4</sub>·LA)]<sup>-</sup>. Their P-nucleophilic site can be subsequently protonated to afford the transient LA-free neutral butterflies *exo,endo*- and *exo,exo*-Cp\*Fe(CO)<sub>2</sub>(η<sup>1</sup>-P<sub>4</sub>H), allowing controllable stepwise metalate-mediated functionalization of P<sub>4</sub>.

Organophosphorus compounds (OPCs) play a crucial role in synthetic chemistry,<sup>[1]</sup> but are typically produced through large-scale halogenation of white phosphorus (P<sub>4</sub> → PCl<sub>3</sub>) and subsequent salt elimination, generating equimolar halogenide waste. However, this is avoidable by direct functionalization of the P<sub>4</sub> tetrahedron. This desirable avenue has been scrutinized for both main-group compounds<sup>[2]</sup> and transition-metal (TM) complexes, ultimately in search of catalytic conversions.<sup>[3]</sup> The challenge is to control the unpredictable reactivity of P<sub>4</sub>. To date, steps invoking reducing neutral metal complexes have

been reported by, for example, the groups of Scheer (Fe),<sup>[4]</sup> Driess (Fe,<sup>[5]</sup> Co,<sup>[6]</sup> and Ni),<sup>[7]</sup> and Cummins (Nb)<sup>[8]</sup> and cations by Peruzzini and co-workers (Fe,<sup>[9]</sup> Ru,<sup>[10]</sup> Rh, and Ir).<sup>[11]</sup> However, in spite of its inherent electrophilic character, reactions of P<sub>4</sub> with TM anions have hardly been considered.

In 2002, Ellis and co-workers provided the first insights by reacting P<sub>4</sub> with a naphthalene-stabilized titanate that afforded the all-inorganic metallocene [(η<sup>5</sup>-P<sub>5</sub>)<sub>2</sub>Ti]<sup>2-</sup> (**A**; Scheme 1).<sup>[12]</sup>



**Scheme 1.** Anionic metal-mediated P<sub>4</sub> functionalization products (counter cations omitted). Cp = C<sub>5</sub>H<sub>5</sub>, Cp\* = C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>, BIAN = 1,2-bis(2,6-diisopropylphenylimino)acenaphthene.

Later, Wolf and co-workers described the formation of iron polyphosphides **B** and **C** through P<sub>4</sub>-aggregation induced by anionic [Cp\*Fe(η<sup>4</sup>-C<sub>10</sub>H<sub>8</sub>)]<sup>-</sup> (Cp\* = C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>),<sup>[13]</sup> and recently the preparation of dinuclear cobalt tetraphosphido complex **D** by reaction of P<sub>4</sub> with [Co(BIAN)(cod)]<sup>-</sup> (BIAN = 1,2-bis(2,6-diisopropylphenylimino)acenaphthene, cod = 1,5-cyclooctadiene).<sup>[14]</sup> The group of Ruiz reported the fragmentation of P<sub>4</sub> into P<sub>2</sub> (**E**), facilitated by the triply bonded molybdenate [Mo<sub>2</sub>Cp<sub>2</sub>(μ-PCy<sub>2</sub>)(μ-CO)<sub>2</sub>]<sup>-</sup> (Cp = C<sub>5</sub>H<sub>5</sub>).<sup>[15,16]</sup>

The marked unpredictability when using metal anions is reminiscent to the often uncontrolled reactions of P<sub>4</sub> with carbanions.<sup>[17]</sup> For this, we developed a selective functionalization strategy by trapping the initial P<sub>4</sub> adduct (using sterically encumbered ArylLi) with Lewis acids to give stabilized bicyclo[1.1.0]tetraphosphabutane anions ([ArylP<sub>4</sub>·LA]<sup>-</sup>; LA = B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or BPh<sub>3</sub>) that can be substituted or fragmented to novel OPCs containing P<sub>4</sub>, P<sub>3</sub>, and P<sub>1</sub> units.<sup>[18]</sup> Herein, we show this approach to also allow the [Cp\*Fe(CO)<sub>2</sub>]<sup>-</sup> anion to functionalize P<sub>4</sub> in a controlled manner, providing the first examples of LA-stabilized TM(η<sup>1</sup>-P<sub>4</sub>)<sup>-</sup> butterfly anions (**1a** and **1b**; Scheme 1),

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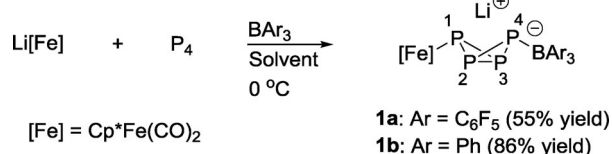
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and report on their P-nucleophilicity by protonation experiments.

To selectively generate anionic TM( $\eta^1$ -P<sub>4</sub>)<sup>-</sup> from P<sub>4</sub>, we reasoned that a stable, bulky metalate with well-defined nucleophilic character would be required, for which the readily available Li[Cp\*Fe(CO)<sub>2</sub>] was considered a good candidate.<sup>[19]</sup> To capture the incipient phosphide, we opted for B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> as strong LA. Indeed, addition of a solution of P<sub>4</sub> in toluene to a cooled (0 °C) mixture of Li[Cp\*Fe(CO)<sub>2</sub>] and B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> instantaneously gave the novel LA-stabilized bicyclo[1.1.0]tetraphosphabutane **1a** ( $\delta^{31}\text{P}\{^1\text{H}\}$ : -65.0 (P1), -107.1 (P4), -340.7 (P2/P3) ppm), which could be isolated in 55% yield as a dark yellow powder (Scheme 2).

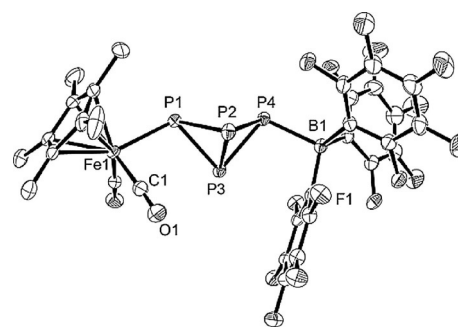


**Scheme 2.** Synthesis of Lewis-acid-stabilized [Cp\*Fe(CO)<sub>2</sub>( $\eta^1$ -P<sub>4</sub>)<sup>-</sup>] butterfly anions. Solvent: toluene for **1a** and THF for **1b**.

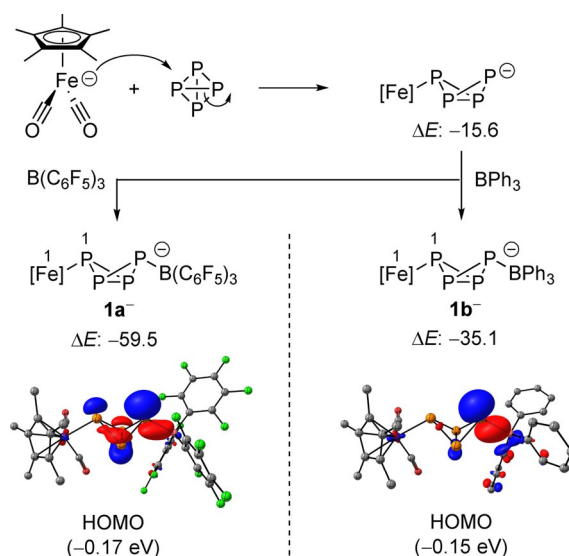
Crystals of **1a**, suitable for single-crystal X-ray diffraction, were grown from Et<sub>2</sub>O after slow (1 min) addition of 12-crown-4. The molecular structure revealed the unprecedented metal-phosphido-borane (Figure 1; [Li(12-crown-4)<sub>2</sub>]<sup>+</sup> counter cation omitted) with a bicyclic P<sub>4</sub> core (P1–P2–P3–P4 98.21(6)°) showing a slightly shorter transannular P2–P3 bond (2.1676(13) Å) compared to the peripheral P1–P2/P1–P3 (2.2324(13)/2.2100(12) Å) and P4–P2/P4–P3 (2.2091(13)/2.2252(13) Å) bonds, as is common for P<sub>4</sub> butterfly-type derivatives.<sup>[18,20,21]</sup> Compound **1a** features a non-symmetric substitution pattern with the tetraphosphide unit being flanked by the Cp\*Fe(CO)<sub>2</sub> moiety (Fe1–P1 2.3192(11) Å) and the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (P4–B1 2.080(4) Å) Lewis acid. The “Lewis” bond is marginally longer than that found in the related organyl-substituted anion Li[Mes\*P<sub>4</sub>-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (P–B 2.064(2) Å),<sup>[18a]</sup> whereas the coordination bond connecting the iron complex is shorter than that observed in the neutral symmetric [(Cp\*Fe(CO)<sub>2</sub>Fe)( $\mu$ , $\eta^1$ -P<sub>4</sub>)] (Fe–P 2.3552(19) Å).<sup>[20a]</sup>

Having established the formation of the [Cp\*Fe(CO)<sub>2</sub>( $\eta^1$ -P<sub>4</sub>)<sup>-</sup>] butterfly anion, we wondered whether the weaker Lewis acid BPh<sub>3</sub> would, likewise, enable its isolation.<sup>[22]</sup> Indeed, addition of Li[Cp\*Fe(CO)<sub>2</sub>] to a THF solution of P<sub>4</sub> and BPh<sub>3</sub> at 0 °C afforded **1b** ( $\delta^{31}\text{P}\{^1\text{H}\}$ : -46.6 (P4), -84.3 (P1), -337.0 (P2/P3) ppm), which was isolated as a brown powder in 86% yield (Scheme 2). Notably, the Li[Cp\*Fe(CO)<sub>2</sub>]/BPh<sub>3</sub> combination in THF results in a higher yield than Li[Cp\*Fe(CO)<sub>2</sub>]/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in toluene (86% and 55%, respectively), likely owing to better solubility of the anions in THF. Its use as a solvent for the synthesis of **1a**, however, is precluded, owing to formation of the reactive THF·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> adduct.<sup>[23]</sup>

Phosphides **1a** and **1b** are the first examples of isolable TM-generated P<sub>4</sub> butterfly anions.  $\omega$ B97X-D/6-311+G(2d,p)//6-31G(d) calculations (Scheme 3) revealed the nucleophilic addi-



**Figure 1.** Molecular structure of **1a<sup>-</sup>** in the crystal (displacement ellipsoids are set at 30% probability; H atoms, [Li(12-crown-4)<sub>2</sub>]<sup>+</sup> counter cation and non-coordinated Et<sub>2</sub>O molecules are omitted for clarity). Selected bond lengths [Å] and angles [°]: P1–P2/P3 2.2324(13)/2.2100(12), P4–P2/P3 2.2091(13)/2.2252(13), P2–P3 2.1676(13), Fe1–P1 2.3192(11), P4–B1 2.080(4), C1–O1 1.151(5); P1–P2–P3–P4 98.21(6).

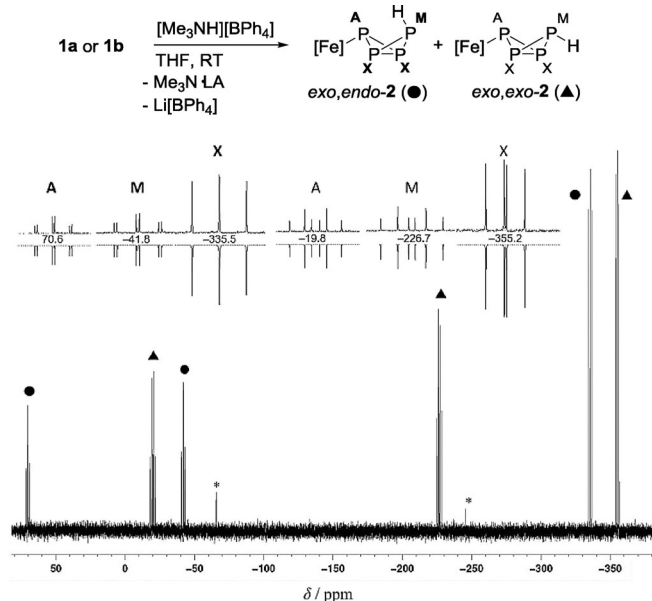


**Scheme 3.** Relative  $\omega$ B97X-D/6-311+G(2d,p)//6-31G(d) energies (in kcal mol<sup>-1</sup>) for the formation of anionic **1a<sup>-</sup>** and **1b<sup>-</sup>** and computed HOMOs (contour value = 0.05). [Fe] = Cp\*Fe(CO)<sub>2</sub>.

tion of [Cp\*Fe(CO)<sub>2</sub>]<sup>-</sup> to P<sub>4</sub> to cause exothermic cleavage ( $\Delta E = -15.6$  kcal mol<sup>-1</sup>) of one P–P bond. The resulting [Cp\*Fe(CO)<sub>2</sub>( $\eta^1$ -P<sub>4</sub>)<sup>-</sup>] “butterfly” anion is stabilized by a significant -59.5 kcal mol<sup>-1</sup> as the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> adduct (**1a<sup>-</sup>**) and by -35.1 kcal mol<sup>-1</sup> ( $\Delta E$ ) with the weaker bonding BPh<sub>3</sub> (**1b<sup>-</sup>**). The stronger bond with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, as compared to BPh<sub>3</sub>, is reflected in the observed 19.3 ppm downfield shift of the <sup>31</sup>P{<sup>1</sup>H} NMR resonance for the P1 atom (**1a** vs. **1b**), owing to the larger electron-withdrawing effect of the fluorinated triarylborane. This difference in inductive effect also leads to a weaker Fe1–P1 bond in the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> adduct. ETS–NOCV analysis revealed a smaller total bonding energy to that in the BPh<sub>3</sub> adduct ( $\Delta\Delta E = 13.7$  kcal mol<sup>-1</sup>)<sup>[24]</sup> and showed a lower contribution for  $\sigma$  donation in the orbital interaction terms (**1a<sup>-</sup>**: -101.6; **1b<sup>-</sup>**: -107.0 kcal mol<sup>-1</sup>;  $\pi$  backdonation **1a<sup>-</sup>**: -10.6; **1b<sup>-</sup>**: -10.9 kcal mol<sup>-1</sup>).<sup>[25]</sup> The highest occupied molecular orbital (HOMO) reflects the lone pair on the boron-coordinated wing-tip P atom and is ex-

pectedly lower in energy for **1a**<sup>−</sup> (−0.17 eV) compared to **1b**<sup>−</sup> (−0.15 eV), suggesting P-nucleophilic character for both.

To probe the utility of anions **1a** and **1b** as nucleophilic reagents, protonation experiments were performed by using the mild acid [Me<sub>3</sub>NH][BPh<sub>4</sub>] in THF.<sup>[26]</sup> Addition of the acid to the most reactive phosphide **1b** (1:1 stoichiometry) showed, in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, the instantaneous formation of two new bicyclo[1.1.0]tetraphosphabutanes, which were identified as the neutral protonated LA-free *exo,endo* and *exo,exo* isomers of Cp\*Fe(CO)<sub>2</sub>(η<sup>1</sup>-P<sub>4</sub>H) (**2**, 1:1.2 ratio; Scheme 4). Simulation of

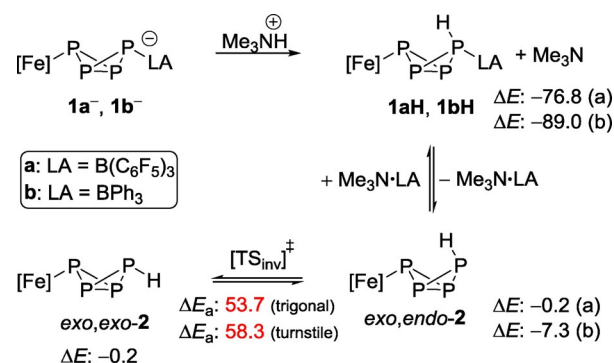


**Scheme 4.** Top: Protonation of **1a** and **1b**. [Fe] = Cp\*Fe(CO)<sub>2</sub>, LA = B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**1a**) or BPh<sub>3</sub> (**1b**). Bottom: <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (162.0 MHz, [D<sub>8</sub>]THF, 297 K) recorded directly after mixing **1b** and [Me<sub>3</sub>NH][BPh<sub>4</sub>]. Insets show expanded experimental and simulated<sup>[27]</sup> (inverted) regions. The resonance signals marked with an asterisk (\*) correspond to unidentified side products.

the <sup>31</sup>P NMR resonances<sup>[27]</sup> confirms the expected AMX<sub>2</sub> spin systems for *exo,endo*-**2** (δ<sub>PA</sub> 70.6, δ<sub>PM</sub> −41.8, δ<sub>PX</sub> −335.5 ppm; <sup>1</sup>J<sub>PA,PX</sub> = −194.5, <sup>1</sup>J<sub>PM,PX</sub> = −198.4, <sup>2</sup>J<sub>PA,PM</sub> = 27.6 Hz) and *exo,exo*-**2** (δ<sub>PA</sub> −19.8, δ<sub>PM</sub> −226.7, δ<sub>PX</sub> −355.2 ppm; <sup>1</sup>J<sub>PA,PX</sub> = −166.4, <sup>1</sup>J<sub>PM,PX</sub> = −149.9, <sup>2</sup>J<sub>PA,PM</sub> = 243.3 Hz). The isomers could be distinguished through the difference in the <sup>2</sup>J<sub>PA,PM</sub> (ΔJ = 215.7 Hz) and <sup>1</sup>J<sub>PH</sub> (145.9 Hz *endo*-PH; 109.3 Hz *exo*-PH) coupling constants. The <sup>1</sup>H NMR spectrum showed a resonance for only the *endo*-PH isomer (−1.14 ppm; <sup>1</sup>J<sub>H,P</sub> = 152.9 Hz). The <sup>11</sup>B{<sup>1</sup>H} NMR spectrum revealed two signals at 27.3 and −8.4 ppm, attributed to the amine–borane adduct Me<sub>3</sub>N·BPh<sub>3</sub> in equilibrium with its constituents and Li[BPh<sub>4</sub>]. The phosphanes decompose within 24 h, owing to a lack of steric protection, which is common for neutral bicyclic tetraphosphanes bearing “small” substituents.<sup>[18a,c]</sup>

Protonation of the less reactive **1a**, likewise, gave a mixture of *exo,endo*-**2** and *exo,exo*-**2** (1:1.2 ratio) with Me<sub>3</sub>N·B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (δ<sup>11</sup>B{<sup>1</sup>H} = −3.0 ppm) as the sole byproduct. We resorted to DFT calculations to obtain more insight into the product formation from the different precursors **1a**<sup>−</sup> and **1b**<sup>−</sup>

(Scheme 5).<sup>[28]</sup> Protonation of the anions by Me<sub>3</sub>NH<sup>+</sup> to give **1aH** or **1bH** was calculated to be quite exothermic (ΔE = −76.8 and −89.0 kcal mol<sup>−1</sup>, respectively), as expected.<sup>[29]</sup> Subsequent cleavage of the *exo*-cyclic P–B bonds by the liberated



**Scheme 5.** Relative ωB97X-D/6-311+G(2d,p)//6-31G(d) energies (in kcal mol<sup>−1</sup>) for the formation of **2**. [Fe] = Cp\*Fe(CO)<sub>2</sub>.

NMe<sub>3</sub> is driven by the formation of the amine–borane adduct and gives *exo,endo*-**2**. This reaction is more exothermic for BPh<sub>3</sub> (**b**, ΔE = −7.3 kcal mol<sup>−1</sup>) than B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**a**, ΔE = −0.2 kcal mol<sup>−1</sup>). The *exo,exo*-**2** isomer was computed to be almost equally stable (ΔE = −0.2 kcal mol<sup>−1</sup>) and is likely formed experimentally through Lewis or Brønsted acid enhanced isomerization<sup>[30]</sup> in light of the high trigonal and turnstile inversion barriers of 53.7 and 58.3 kcal mol<sup>−1</sup>, respectively.<sup>[31]</sup>

The selective protonation at the wing-tip P atoms of the complexed P<sub>4</sub> anions **1a** and **1b** confirms their P-nucleophilic character and provides a simple route to hitherto scarce non-symmetrical neutral TM-complexed P<sub>4</sub> derivatives. The reactivity is analogous to the organyl-substituted congeners and should, therefore, be extendable to alkylations and possibly [3+1] fragmentations, on which we reported recently.<sup>[18c]</sup> The present report lies the foundation for the isolation of new TM-mediated P<sub>4</sub>-functionalized products.

In conclusion, reacting anionic Li[Cp\*Fe(CO)<sub>2</sub>] with P<sub>4</sub> in the presence of either the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or BPh<sub>3</sub> Lewis acid provides facile access to unique metal-substituted bicyclo[1.1.0]tetraphosphabutane anions. Their P-nucleophilic site can be protonated, affording the novel transient LA-free tetraphosphanes *exo,endo*- and *exo,exo*-Cp\*Fe(CO)<sub>2</sub>(η<sup>1</sup>-P<sub>4</sub>H). The controlled and selective formation of these intriguing new anionic and neutral derivatives enables the selective functionalization of white phosphorus by anionic metalates to be explored.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** anions · iron · Lewis acids · P<sub>4</sub> functionalization · white phosphorus

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