Catalytic Intermediates

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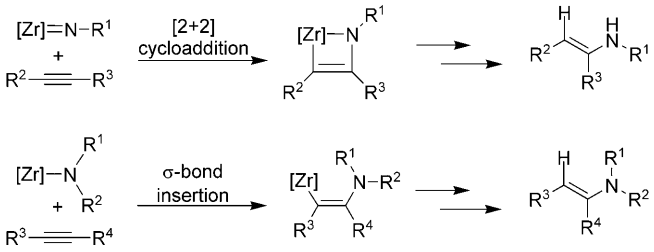
# Isolation of Catalytic Intermediates in Hydroamination Reactions: Insertion of Internal Alkynes into a Zirconium–Amido Bond**

*David C. Leitch, Courtney S. Turner, and Laurel L. Schafer**

Metal-catalyzed hydroamination, a direct and atom-economic approach for the formation of C–N bonds, is becoming an increasingly powerful method in organic synthesis.[1] This catalytic addition of N–H bonds across C–C unsaturated bonds allows for the preparation of complex nitrogen-containing compounds using readily available and inexpensive starting materials. Furthermore, these reactions proceed without the need for stoichiometric amounts of reagents, or the generation of waste by-products. There have been a staggering number of catalytic systems developed for this reaction, exhibiting a corresponding high degree of mechanistic diversity.[1–8] In particular, the hydroamination of alkynes, allenes, and alkenes using Group 4 metal catalysts has been proposed to occur through a [2+2] cycloaddition between the unsaturated substrate and a metal–imido bond.[3] More recently, proposals of a σ-bond insertion of the unsaturated substrate into a metal–amido bond have been asserted for select cationic[4] and neutral[5] Group 4 metal catalysts, akin to that established for Group 3 and lanthanide metals[6] (Scheme 1). The vast majority of previous kinetic, synthetic, and computational studies to determine the mechanism for hydroamination reactions using Group 4 metals supports the [2+2] mechanism.[1,3,7,8] A compelling piece of evidence for this proposal is that catalytically relevant azametallacycles, resulting from stoichiometric [2+2] cycloadditions between Group 4 metal–imido complexes and C–C unsaturated bonds, have been isolated and structurally characterized.[3c,7] As a consequence of this imido-mediated catalytic cycle, nearly all Group 4 metal catalysts can use only primary amines as substrates.[1,3,8]




***Scheme 1.*** Two pathways for zirconium-catalyzed alkyne hydroamination.

A small number of Group 4 metal systems have been reported that exhibit contrasting reactivity.[4,5] Cationic zirconium species, which are isovalent with Group 3 and lanthanide metal complexes, can successfully cyclize secondary aminoalkene substrates;[4] however, these same systems are ineffective with primary aminoalkenes. Notably, there are a limited number of neutral, sterically accessible zirconium catalysts that are able to catalyze hydroamination reactions using both primary and secondary amines.[5] A detailed synthetic and kinetic study of "constrained-geometry" catalysts by Stubbert and Marks provides compelling evidence that a σ-bond insertion mechanism is operative,[5c] which is in contrast to nearly every other neutral Group 4 metal system reported to date.[1,3,8]

While stoichiometric insertions of polar, electrophilic carbon–heteroatom multiple bonds into titanium- and zirconium–amido bonds are well established,[9] those of nonpolar C–C unsaturated bonds are exceedingly rare. There is a single characterized example of alkyne insertion into a Group 4 metal–nitrogen bond, involving the highly strained [$Cp_2Zr(N_2Ph_2)$] metallacycle (Cp = cyclopentadienyl), reported by Bergman and co-workers in 1990.[10] Apart from this, there is only one characterized example of electron-rich alkyne insertion into an unstrained amido bond of any metal, which was reported by Odom and co-workers for a $d^2$-molybdenum(IV) center.[11] The rarity of these electron-rich, C–C multiple bond insertions into metal–nitrogen bonds can be partly explained by the electronic nature of the $d^0$-metal–amido linkage. Coulombic repulsion between the formal metal–nitrogen double bond and the incoming C–C multiple bond results in a substantial kinetic barrier to insertion.[12] Thermodynamically, these insertion reactions are estimated to be thermoneutral or only slightly exothermic,[1,13] owing to the strength of the Zr–N bond.[14]

During the course of our own research on hydroamination reactions, we have identified a ureate-supported zirconium precatalyst (**1**) that is highly effective for the hydroamination of alkynes and alkenes with both primary and secondary amines.[5a] Herein, we report the isolation and characterization of vinylamine complexes (**2a–c**) resulting from electron-rich, nonpolar alkyne insertion into a Zr–N bond of **1** [Eq. (1)]. These represent the first characterized examples of stoichiometric C–C multiple bond insertion into an unstrained, $d^0$-metal–amido bond. Not only are **2a–c** derived

[*] D. C. Leitch, C. S. Turner, Prof. L. L. Schafer
Department of Chemistry, University of British Columbia
2036 Main Mall, Vancouver, B.C., V6T 1Z1 (Canada)
Fax: (+1) 604-822-2847
E-mail: schafer@chem.ubc.ca

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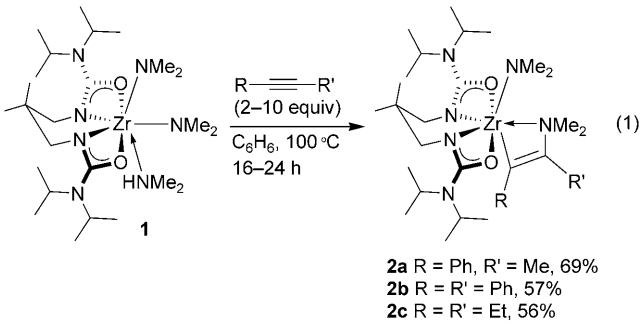



(1)

from an active hydroamination precatalyst (**1**), they are also themselves catalytically competent.

As part of our efforts to determine the source of the unique catalytic activity of **1** relative to other Group 4 metal systems, we undertook a structural analysis of the precatalyst (Figure 1). The seven-coordinate complex exhibits distorted

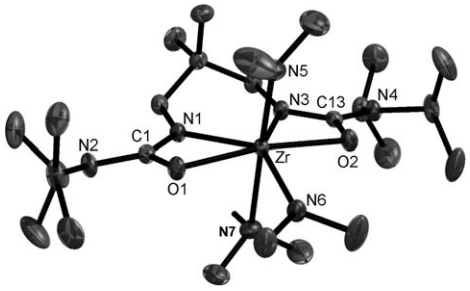
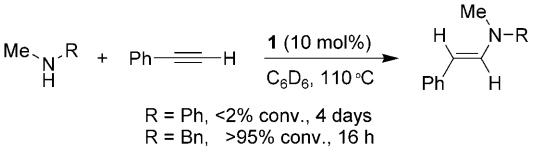



***Figure 1.*** ORTEP representation of the molecular structure of **1** (ellipsoids drawn at 50% probability, H atoms except that on N7 are omitted). Selected bond lengths (Å) and angles (°): Zr–N1 2.280(1), Zr–N5 2.092(2), Zr–N6 2.135(1), Zr–N7 2.503(2), Zr–O1 2.240(1), N1-Zr-O1 57.91(5).

pentagonal bipyramidal geometry, with the bis(ureate) ligand located in the equatorial plane. The dimethylamido ligands are oriented *cis* to the zirconium center, and the seventh coordination site is occupied by a neutrally bound dimethylamine group that is oriented *trans* to the axial amido ligand. An examination of the geometrical parameters reveals a remarkably longer Zr–$NMe_2$ bond of 2.135(1) Å for the equatorial amido ligand, while the axial Zr–$NMe_2$ bond is 2.092(2) Å. Structurally analogous seven-coordinate amidate and sulfonamidate complexes have Zr–N bond lengths that range between 2.06–2.07 Å for both axial and equatorial amido ligands.[8b,h]

The length of this equatorial amido bond cannot be rationalized in steric terms,[15] nor can it be explained by electron delocalization with an adjacent unsaturated organic group.[16] Instead, we propose that this elongation is a result of the reduced π-bonding character in the equatorial Zr–$NMe_2$ linkage, which is in the same plane as the other four donors of the ureate ligand. In contrast, the axial amido ligand is oriented to maximize π-orbital overlap. We suggest that the decreased metal–ligand π bonding of the equatorial amido ligand in this case results in a more nucleophilic nitrogen atom *cis* to the axial site accessible for neutral ligand coordination. Our hypothesis is that during the hydroamination catalysis, coordination of the alkyne substrate occurs in the axial position on the electrophilic, sterically accessible zirconium metal center. This coordinated species would then facilitate the intramolecular nucleophilic attack of the alkyne substrate by the electron-rich equatorial amido nitrogen atom, thus resulting in C–N bond formation and formal σ-bond insertion.[11a]

This hypothesis is supported by comparing the use of aryl/alkyl and dialkyl amines in hydroamination reactions catalyzed by **1** [Eq. (2)]. *N*-methylaniline is ineffective as a substrate for alkyne hydroamination, and gives none of the desired product under catalytic conditions. Here, we suggest that delocalization of the nitrogen lone pair of electrons into the aromatic system disfavors nucleophilic attack, thereby preventing the insertion. In contrast, dialkyl-substituted amines are transformed efficiently into the anticipated enamine products.[5a] Furthermore, to the best of our knowledge, no catalytic intermolecular hydroamination system that is proposed to operate via σ-bond insertion is able to use *N*-aryl amines as substrates.[1]




(2)

To test our mechanistic model, we have examined the feasibility of stoichiometric alkyne insertion into the Zr–$NMe_2$ bonds of complex **1**. Treatment of **1** with an excess amount of 1-phenyl-1-propyne, diphenylacetylene, or 3-hexyne at 100 °C resulted in the formation of vinylamine complexes **2a–c** in moderate yields after recrystallization [Eq. (1)].[17] The compounds are crystalline solids, and are therefore easily isolated, purified, and characterized. The NMR spectroscopic features of **2a–c** are very similar to one another, and are consistent with the molecular formulations in Equation (1). Upon conversion from **1**, the protons of the *gem*-dimethyl moiety of the ureate ligand become inequivalent, as do the adjacent methylene protons, which resonate as a diagnostic AB quartet in all three cases. Two signals are observed for the methyl protons on the $NMe_2$ groups, one for the axial dimethylamido ligand, and one for the new alkenyl(dimethylamino) ligand. Complex **2a** is formed as a single isomer, with no indication of the presence of the other insertion regioisomer. The $^{13}C$ NMR spectra of **2a–c** are devoid of any alkynyl carbon signals; in each case, a new resonance near $\delta = 180$ ppm is observed, which corresponds to the carbon atom directly attached to the zirconium center, as has been previously characterized for other metallacyclic $sp^2$-hybridized C–Zr bonds.[3c] Electron impact mass spectrometry enables the observation of signals corresponding to molecular ions and diagnostic fragments, and finally combustion analyses are consistent with the empirical formulae (see the Supporting Information).

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Single crystals of **2a** and **2b** were subject to X-ray crystallographic analysis to confirm the structural assignment.[18] The molecular structure of **2a** is shown in Figure 2.

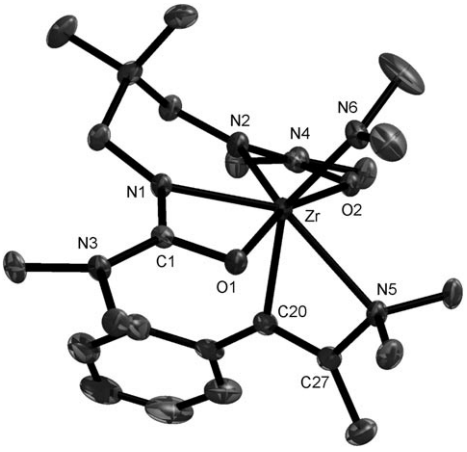
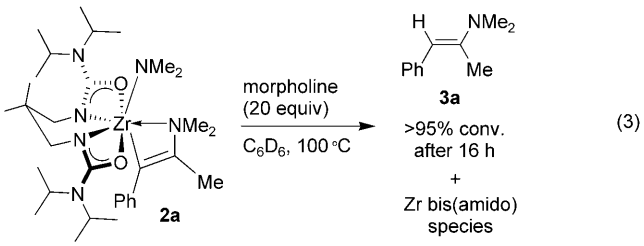



***Figure 2.*** ORTEP representation of the molecular structure of **2a** (ellipsoids drawn at 50% probability, H atoms and methyl groups from isopropyl groups are omitted). Selected lengths (Å) and angles (°): Zr–N1 2.208(1), Zr–N5 2.443(1), Zr–N6 2.087(2), Zr–C20 2.324(2), Zr–O1 2.200(1), C20–C27 1.326(2), N1-Zr-O1 59.28(5), N5-Zr-C20 58.25(6).

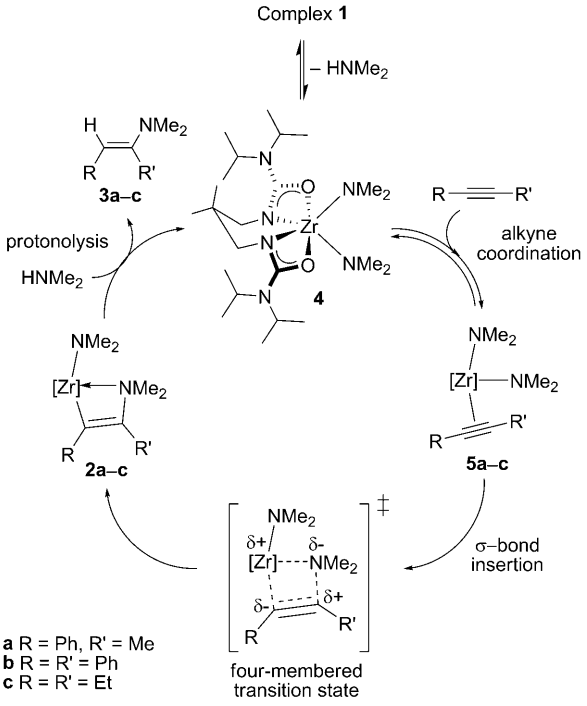
Both complexes have analogous features, and have undergone only minimal geometric reorganization from the parent zirconium species. The structure of **2a** reveals which regioisomer is formed, and is consistent with the previously determined regioselectivity of the hydroamination between 1-phenyl-1-propyne and morpholine catalyzed by **1**.[5a] The observed regioselectivity is also consistent with the results previously observed for other hydroamination systems that employ a formal σ-bond insertion mechanism.[2f,6b] The observed geometry of **2a** and **2b** suggests that the alkyne substrate inserts preferentially into the weaker equatorial Zr–N bond, as proposed.[19] The C20–C27 bond length of 1.326(2) Å is consistent with a C–C double bond, while the C27–N5 bond length of 1.477(3) Å indicates a C–N single bond. The long Zr–N5 bond length of 2.443(1) Å confirms that the N donor of the vinylamine group is bound to the zirconium center in a neutral fashion.

In situ monitoring of the insertion reactions by $^1$H NMR spectroscopy reveals not only the nearly quantitative formation of the organometallic products, but also 0.3 to 0.6 equivalents of free *N*,*N*-dimethylenamines **3a–c**. To confirm that enamine products can be formed through aminolysis of the Zr–C bond of **2a**, and to confirm that the isolated vinylamine complexes are catalytically viable for alkyne hydroamination, complex **2a** was treated with a large excess of morpholine at 100 °C [Eq. (3)]. Complete conversion into the enamine **3a** was observed in less than 16 hours. Finally, complex **2a** is itself a viable hydroamination precatalyst. A catalyst loading of 10 mol% of **2a** resulted in the hydroamination of phenylacetylene with morpholine in 16 hours at 100 °C; which corresponds to the same reactivity previously reported using precatalyst **1**.[5a]




(3)

All of the above experimental observations can be rationalized by the proposed mechanism shown in Scheme 2.[20] Dissociation of dimethylamine from **1** would




***Scheme 2.*** Proposed mechanistic pathway leading to the formation of isolated intermediates **2a–c** and observed enamines **3a–c**.[20]

give a coordinatively unsaturated intermediate **4**, which could accommodate alkyne coordination in the axial position to regenerate a seven-coordinate intermediate. This coordination would then activate the alkyne toward insertion by lowering the energy of the π* LUMO, and positioning it in close proximity to the reactive equatorial amido ligand. Nucleophilic attack by the lone pair of electrons on the nitrogen atom of the equatorial amido ligand onto the coordinated alkyne could then form the vinylamine complexes **2a–c** through a formal σ-bond insertion. In the presence of the dimethylamine unit liberated to form **4**, rapid aminolysis of the Zr–C bond would give the observed enamines **3a–c**, and regenerate **4**. As the soluble $HNMe_2$ is consumed in the stoichiometric reactions, the cycle would become arrested, thus enabling the isolation of complexes **2a–c**. Alternatively, in the presence of an excess amount of a dialkylamine substrate, such as morpholine, efficient turnover

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is observed and results in the catalytic synthesis of the enamine.

In summary, we have identified, isolated, and characterized key catalytic intermediates in the intermolecular hydroamination reaction of alkynes with a highly active zirconium catalyst system. The vinylamine complexes **2a**–**c** have been isolated and are the first examples of formal nonpolar C–C multiple bond insertion into unstrained $d^0$-metal–nitrogen bonds. Furthermore, these vinylamine complexes are themselves catalytically competent. According to our mechanistic hypothesis the unique bonding environment supported by the electron-rich, tethered ureate ligand is able to reduce the multiple bond character of the equatorial amido ligand, consequently the nitrogen lone pair of electrons is capable of nucleophilic attack on the coordinated alkyne substrate.[20] Kinetic, synthetic, and computational studies are currently underway to provide valuable insight into the details of this process, with the goal of effectively designing the next generation of Group 4 metal hydroamination catalysts.

## Experimental Section

Synthesis of complexes: **1** (100.0 mg, 0.173 mmol) and the alkyne (0.346 mmol for **2a** and **2b**, 1.73 mmol for **2c**) were dissolved in benzene (1 mL). The solution was heated to 100 °C for 16 h (for **2a** and **2b**) or 24 h (for **2c**) prior to solvent removal under vacuum. The residue was recrystallized from pentane at −35 °C to give 78.0 mg (69 %) of **2a**, 70.0 mg (57 %) of **2b**, 59.3 mg (56 %) of **2c**.

Characterization of **2a**: $^1$H NMR ($C_7D_8$, 400 MHz) $\delta = 0.77$ (3H, s, $CH_3$), 1.09 (3H, s, $CH_3$), 1.22 (12H, d, $J = 8.0$ Hz, 2x$CH(CH_3)_2$), 1.24 (12H, d, $J = 8.0$ Hz, 2x$CH(CH_3)_2$), 1.66 (3H, s, [Zr]–C(Ph)=C-($CH_3$)($NMe_2$)), 2.81 (6H, s, C=C($CH_3$)(N($CH_3)_2$)), 3.07 (4H, AB q, $J = 10.0$ Hz, 2x$Me_2C(CH_2)$N), 3.29 (6H, s, [Zr]–N($CH_3)_2$), 3.57 (4H, sept, $J = 8.0$ Hz, 4x$CH(CH_3)_2$), 6.93 (3H, m, 3xPh-*H*), 7.24 ppm (2H, m, 2xPh-*H*); $^{13}$C NMR ($C_7D_8$, 100 MHz, $CH_2$ and *C* determined from DEPT experiments) $\delta = 6.5$, 21.8, 22.1, 22.2, 27.0, 36.3 (*C*), 43.6, 45.4, 46.3, 57.3 ($CH_2$), 121.4, 124.8, 127.3, 145.6 (*C*), 149.8 (*C*), 168.5 (*C*), 182.2 ppm (*C*); MS(EI) *m*/*z* 648 ($M^+$), 604 ([LZr–C(Ph)=C(Me)-($NMe_2$)]$^+$), 488 ([LZr$NMe_2$]$^+$); Elemental analysis calcd for $C_{32}H_{58}N_6O_2Zr$: C 59.12, H 8.99, N, 12.93; found: C 59.31, H 8.91, N 12.76.

Characterization of **2b**: $^1$H NMR ($C_7D_8$, 400 MHz) $\delta = 0.83$ (3H, s, $CH_3$), 1.16 (3H, s, $CH_3$), 1.25 (12H, d, $J = 6.7$ Hz, 2x$CH(CH_3)_2$), 1.28 (12H, d, $J = 6.7$ Hz, 2x$CH(CH_3)_2$), 2.92 (6H, s, C=C($CH_3$)(N($CH_3)_2$)), 3.17 (4H, AB q, $J = 11.2$ Hz, 2x$Me_2C(CH_2)$N), 3.32 (6H, s, [Zr]–N($CH_3)_2$), 3.61 (4H, sept, $J = 6.7$ Hz, 4x$CH(CH_3)_2$), 6.75 (1H, t, $J = 7.3$ Hz, 1xPh-*H*), 6.90 (2H, d, $J = 7.9$ Hz, 2xPh-*H*), 6.96 (1H, t, $J = 7.3$ Hz, 1xPh-*H*), 7.02–7.09 (4H, m, 4xPh-*H*), 7.26 ppm (2H, d, $J = 6.8$ Hz, 2xPh-*H*); $^{13}$C NMR ($C_7D_8$, 100 MHz, $CH_2$ and *C* determined from DEPT experiments) $\delta = 21.8$, 21.9, 22.3, 27.2, 36.4 (*C*), 44.9, 45.3, 46.3, 57.5 ($CH_2$), 121.7, 125.7, 126.3, 127.0, 127.4, 130.8, 135.2 (*C*), 148.3 (*C*), 149.4 (*C*), 168.5 (*C*), 183.4 ppm (br, *C*); MS(EI) *m*/*z* 710 ($M^+$), 666 ([LZr–C(Ph)=C(Ph)($NMe_2$)]$^+$), 488 ([LZr$NMe_2$]$^+$); Elemental analysis calcd for $C_{37}H_{60}N_6O_2Zr$: C 62.40, H 8.49, N 11.80; found: C 62.76, H 8.52, N 11.55.

Characterization of **2c**: $^1$H NMR ($C_6D_6$, 400 MHz) $\delta = 1.01$ (3H, s, $CH_3$), 1.27 (3H, t, $J = 7.6$ Hz, $CH_2CH_3$), 1.32 (24H, m, 4x $CH(CH_3)_2$), 1.35 (3H, s, $CH_3$), 1.40 (3H, t, $J = 7.6$ Hz, $CH_2CH_3$), 2.24 (2H, q, $J = 7.6$ Hz, $CH_2CH_3$), 2.55 (2H, q, $J = 7.6$ Hz, $CH_2CH_3$), 2.87 (6H, s, C=C($CH_3$)(N($CH_3)_2$)), 3.27 (2H, d, $J = 11.2$ Hz, $Me_2C(CH_2)$N), 3.42 (2H, d, $J = 11.2$ Hz, $Me_2C(CH_2)$N), 3.51 (6H, s, [Zr]–N($CH_3)_2$), 3.67 ppm (4H, sept, $J = 6.8$ Hz, 4x$CH(CH_3)_2$); $^{13}$C NMR ($C_6D_6$, 100 MHz, $CH_2$ and *C* determined from DEPT experiments) $\delta = 15.2$ ($CH_2$), 16.3, 16.8, 21.9, 22.1, 22.6, 26.7, 27.6,($CH_2$), 36.7 (*C*), 44.6, 45.8, 46.3, 57.9 ($CH_2$), 152.4 (*C*), 168.9 (*C*), 184.2 ppm (*C*); MS(EI) *m*/*z* 614 ($M^+$), 570 ([LZr–C(Et)=C(Et)($NMe_2$)]$^+$), 488 ([LZr$NMe_2$]$^+$); Elemental analysis calcd for $C_{29}H_{60}N_6O_2Zr$: C 56.54, H 9.82, N 13.64; found: C 56.20, H 10.14, N 13.85.

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[19] Alternatively, this ligand arrangement could result from isomerization to a thermodynamic product via a six-coordinate intermediate.

[20] A reviewer has pointed out that the reduced Zr–N π bonding proposed for complex **1** may not be common to intermediates **4** and **5**. An alternate electronic rationale for the observed reactivity, such as a formal [2+2] cycloaddition between the alkyne and the π contribution to the Zr–N bond, cannot therefore be ruled out. Computational work is currently underway to address these questions.

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