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Kylin A. Emhoff
Cleveland State University

Ahmed M.H. Salem
Cleveland State University

Lakshmi Balaraman
Cleveland State University

Drew M. Kingery
Cleveland State University

W. Christopher Boyd
Cleveland State University, w.c.boyd59@csuohio.edu

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Allylic amination and carbon–carbon double bond transposition catalyzed by cobalt(II) azodioxide complexes

Kylin A. Emhoff, Ahmed M.H. Salem, Lakshmi Balaraman, Drew M. Kingery, W. Christopher Boyd*

Department of Chemistry, Cleveland State University, 2121 Euclid Avenue, Cleveland, OH 44114, United States

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ABSTRACT

The unusual cobalt(II) diphenylazodioxide complex salts $[\text{Co}(\text{az})_4](\text{PF}_6)_2$ and $[\text{Co}(\text{bpy})(\text{az})_2](\text{PF}_6)_2$ have been shown to catalyze the allylic amination/C–C double bond transposition reaction of 2-methyl-2-pentene with PhNHOH, with a turnover number of about 4. The mechanism is proposed to involve a nitroso-ene-like transfer of a PhNO moiety from the azodioxide ligand to the alkene, followed by reduction of the organic product to yield a cobalt(III) intermediate, which is itself reduced back to cobalt(II) by PhNHOH, regenerating PhNO. Hetero-Diels-Alder trapping experiments suggest that an “off-metal” mechanism, in which PhNO is released from the cobalt complexes and reacts with the alkenes, is operative, in contrast to an “on-metal” mechanism observed by Nicholas and coworkers for $[\text{Fe}(\text{az})_3](\text{FeCl}_4)_2$.

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1. Introduction

The addition of nitrogen-containing functional groups to unsaturated organic molecules is an important step in complex molecule synthesis, and can consist either of hydroamination across a double or triple bond, or an overall oxidative process. Transition metal complexes have been used to catalyze both types of reaction [1]. An important subtype of these oxidative processes is those in which allylic alkenes are aminated, yielding products in which the C–C bond has migrated from its position in the starting material. A variety of intramolecular allylic aminations, resulting in cyclic products, have been shown to be mediated or catalyzed by Pd(II) species: Hegedus and coworkers [2,3] rendered these reactions catalytic with benzoquinone as the stoichiometric oxidant [3], while Andersson and coworkers [4], Larock and coworkers [5], and Stahl and coworkers [6] all used O_2 as the stoichiometric oxidant.

An alternative type of allylic amination reaction involves the reaction of a nitroso compound with an alkene bearing allylic hydrogens, in a variant of the well-known Alder ene reaction [7] with the nitroso compound acting as enophile. These reactions yield allylic hydroxylamine products [8,9], and an example nitroso-ene reaction on a simple trisubstituted alkene with a nitrosoarene enophile (ArNO) is shown in Fig. 1 below. The major product of such reactions

usually results from hydrogen abstraction from the carbon labeled *twix*, as opposed to the *twin* or *lone* carbons; this preference has been theorized to arise from a mechanism involving diradical intermediates [10], though it has been proposed that some nitroso-ene reactions are concerted [11].

Nitroso-ene and related reactions need not be metal-mediated or metal-catalyzed, as many nitroso compounds will react directly with alkenes bearing allylic hydrogens. Transition metal complexes have, however, been shown to enable nitroso-ene-like reactions whose organic product is an allylic secondary amine, as opposed to a hydroxylamine. These reactions often involve metal complexes of nitrosoarenes as catalysts or intermediates; such complexes have been extensively reviewed [12–14]. Sharpless, Ibers, and coworkers showed that Mo(VI) complexes of η^2 -ArNO ligands could stoichiometrically transfer an ArN moiety to the allylic position of an alkene with concomitant C–C double bond transposition, with the ArNO oxygen atom becoming an oxido ligand on Mo [15]. Nicholas and coworkers demonstrated that this allylic amination/C–C double bond transposition reaction could be performed with an alkene and phenylhydroxylamine (PhNHOH) as reactants, catalyzed by the Mo(VI) complex $\text{Mo}(\text{O})_2(\text{dipic})(\text{HMPA})$, where dipic = pyridine-2,6-dicarboxylate and HMPA = hexamethylphosphoramide. This reaction was proposed to initially generate an allylic hydroxylamine and an Mo(IV) complex, with oxo transfer from this hydroxylamine to Mo(IV) yielding the final organic product and regenerating the Mo(VI) catalyst. Mechanistic experiments suggested the intermediacy of free nitrosobenzene (PhNO), generated *in situ* by oxidation of PhNHOH [16].

* Corresponding author.

E-mail addresses: k.Emhoff@vikes.csuohio.edu (K.A. Emhoff), a.m.salem@vikes.csuohio.edu (A.M.H. Salem), w.c.boyd59@csuohio.edu (W.C. Boyd).

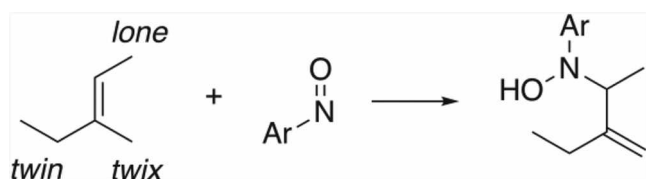


Fig. 1. Regioselectivity of the nitroso-ene reaction.

Metal-catalyzed nitroso-ene-type reactions can be mechanistically classified based on whether they are, in the terminology of Johannsen and Jørgensen [17], “off-metal,” with a free nitroso compound generated as an intermediate, or “on-metal,” with the nitroso compound bound to a transition metal when it reacts with the alkene substrate. Off-metal reactions tend to be more common, but which class of mechanism applies can vary substantially based on the ligands present: an off-metal mechanism was proposed for allylic amine formation catalyzed by Fe(phthalocyanine) [18], as for allylic amine formation catalyzed by $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ [19]. Srivastava and coworkers, however, obtained experimental support for an on-metal mechanism for allylic amine formation with $[\text{Cu}(\text{NMe})_4]\text{PF}_6$ as the catalyst. In particular, when these reactions were run in the presence of 2,3-dimethyl-1,3-butadiene, the hetero-Diels-Alder adduct of this diene and PhNO was not formed, indicating that free PhNO was not an intermediate [20–22].

An unusual instance of an on-metal allylic amination/double bond transposition reaction was discovered by Nicholas and coworkers, who studied amination of alkenes by PhNHOH with FeCl_2 as precatalyst. They isolated the Fe(II)/Fe(III) complex salt $[\text{Fe}(\text{az})_3](\text{FeCl}_4)_2$, where az = the azodioxide *cis*-Ph(O)NN(O)Ph, the dimer of PhNO, from the amination reaction mixtures, and showed that it was a competent catalyst itself for the amination reactions [23,24]. They proposed that the trigonal prismatic Fe(II) cation $[\text{Fe}(\text{az})_3]^{2+}$ was the active aminating agent, with no free PhNO generated, based on the lack of a Diels-Alder product found when the reaction was carried out in the presence of 2,3-dimethyl-1,3-butadiene. Instead, they proposed that the nitroso-ene-like reaction step occurs between a PhNO moiety from a κ^1 -azodioxide ligand (with one oxygen atom unbound) and the alkene, coordinated to Fe in an η^2 fashion, as shown in Fig. 2. The allylic hydroxylamine product initially formed is deoxygenated by Fe(II) species, which are oxidized to Fe(III) in the process and then later reduced back to Fe(II) by the PhNHOH reactant [24].

Azodioxide complexes such as $[\text{Fe}(\text{az})_3](\text{FeCl}_4)_2$ are exceedingly rare, perhaps because of the tendency of PhNO to exist as *cis*-Ph(O)NN

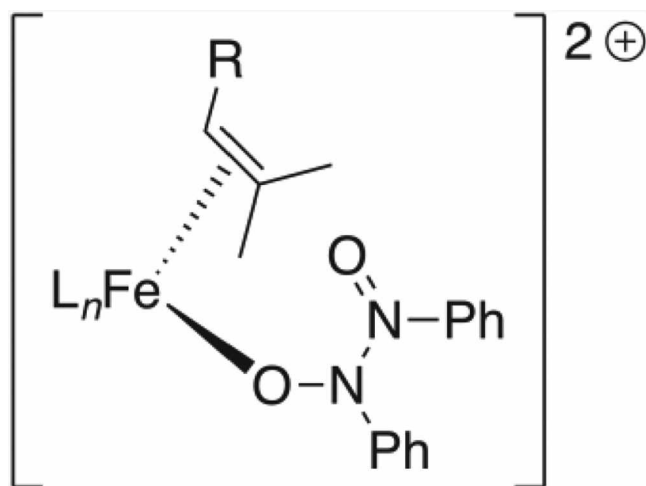


Fig. 2. Proposed intermediate from which a nitroso-ene-like reaction occurs in Nicholas and coworkers' Fe-catalyzed amination.

(O)Ph in the solid state, but as monomeric PhNO in solution [25,26]. Thus far, only five azodioxide complexes have been structurally characterized: $[\text{Fe}(\text{az})_3](\text{FeCl}_4)_2$ [23,24], the main-group, Ca(II) complex salt $[\text{Ca}(\text{az})(\text{H}_2\text{O})_2(\text{THF})_3]_2$, prepared by Hanusa and coworkers [27], the d^0 , Sc(III) complex $[\text{Sc}(\text{az}')(\text{H}_2\text{O})_2(\text{OTf})_3]$, where $\text{az}' = \text{cis}$ -(2-MeOC₆H₄)(O)NN(O)(2-MeOC₆H₄) and Tf = F₃CSO₂, prepared by Whiting and coworkers [28], and the d^7 , Co(II) complex salts $[\text{Co}(\text{az})_4](\text{PF}_6)_2$ and $[\text{Co}(\text{bpy})(\text{az})_2](\text{PF}_6)_2$, where bpy = 2,2'-bipyridyl, recently reported by our group [29,30], whose structures are shown in Fig. 3 below.

While the reactivity of $[\text{Ca}(\text{az})(\text{H}_2\text{O})_2(\text{THF})_3]_2$ with organic substrates has not, to the best of our knowledge, been explored, Whiting and coworkers demonstrated [28] that 1,3-cyclohexadiene reacts with $[\text{Sc}(\text{az}')(\text{H}_2\text{O})_2(\text{OTf})_3]$ to form its hetero-Diels-Alder adduct with (2-MeOC₆H₄)NO. Interestingly, this reaction is no faster than that of 1,3-cyclohexadiene and (2-MeOC₆H₄)NO in the absence of any metal, indicating an off-metal process in which reversible dissociation of azodioxide from $[\text{Sc}(\text{az}')(\text{H}_2\text{O})_2(\text{OTf})_3]$, and equilibrium between the azodioxide and the nitrosoarene monomer, is responsible for the dienophilic reactivity.

The unusual coordination geometry of $[\text{Co}(\text{az})_4](\text{PF}_6)_2$ and $[\text{Co}(\text{bpy})(\text{az})_2](\text{PF}_6)_2$, namely tetragonal for $[\text{Co}(\text{az})_4]^{2+}$ and trigonal prismatic for $[\text{Co}(\text{bpy})(\text{az})_2]^{2+}$, combined with their pro-apoptotic activity toward SK-HEP-1 liver cancer cells, demonstrated in collaboration with Zhou and coworkers [31], prompted us to test their ability to catalyze allylic amination/double bond transposition reactions of the sort catalyzed by $[\text{Fe}(\text{az})_3](\text{FeCl}_4)_2$. We here demonstrate that both complexes are able to catalyze the reaction of 2-methyl-2-pentene with PhNHOH. However, trapping experiments indicate that, in contrast to $[\text{Fe}(\text{az})_3](\text{FeCl}_4)_2$ -catalyzed aminations, an off-metal mechanism is operative, with free PhNO generated as an intermediate.

2. Experimental

2.1. General experimental considerations

Catalytic reactions were set up under anaerobic and anhydrous conditions (a dry nitrogen atmosphere) in an MBraun Labstar Pro glovebox. Glassware was dried in an oven at 160 °C before use. NMR spectra were acquired using a Bruker Avance III 400 MHz spectrometer. Reaction solvents were deoxygenated by sparging with dry nitrogen, and then dried via passage through activated alumina in an MBraun MB-SPS solvent purification system and stored in the glovebox. Column chromatography was performed under air in a fume hood. The cobalt azodioxide complexes $[\text{Co}(\text{az})_4](\text{PF}_6)_2$ and $[\text{Co}(\text{bpy})(\text{az})_2](\text{PF}_6)_2$ were prepared as previously described by our group [29]. Other reagents were obtained from commercial suppliers (Sigma-Aldrich, Fisher). Liquid reagents were degassed via the freeze-pump-thaw method and dried over activated 4 Å molecular sieves [32]. GC-MS analysis of reaction mixtures were performed on an Agilent GC-MS with a nonpolar column.

2.2. Allylic amination/C—C double bond transposition reactions

In the glovebox, 0.073 mmol cobalt catalyst (10 mol% based on the limiting reagent, PhNHOH) was dissolved in 2.5 mL acetonitrile and added to a Schlenk tube equipped with a magnetic stir bar. To this solution was added 1.6 mmol alkene (2-methyl-2-pentene or 2-methyl-2-hexene), then 0.73 mmol phenylhydroxylamine dissolved in 5 mL acetonitrile, for a total volume of 7.5 mL. The Schlenk tube was tightly sealed with a Teflon stopcock, removed from the glovebox, and heated in an oil bath at 75 °C for 72 h. The Schlenk tube was then allowed to cool to room temperature, after which the solvent was removed under reduced pressure, yielding a brown solid, which was extracted into diethyl ether.

GC-MS analysis was performed on a small sample of this diethyl ether solution after passing it through a miniature column consisting of about 5 cm silica gel above a cotton ball in a Pasteur pipet, in order



Fig. 3. Structures of cobalt azodioxide complexes.

to remove nonvolatile metal-containing species. Preparative column chromatography was performed using a silica column using a petroleum ether/diethyl ether gradient, and the fractions containing the allylic amine product were identified by thin layer chromatography and UV light (254 nm). The product-containing fractions were combined and the solvent removed under reduced pressure to yield the allylic amine as a yellow oil. Identity and purity of the allylic amines were confirmed by ^1H NMR spectroscopy in CDCl_3 and comparison with literature spectral data [24].

2.3. Diels-Alder trapping experiment to determine presence of nitrosobenzene

The procedure for allylic amination/C–C double bond transposition reactions described above was followed, but with no phenylhydroxylamine present and 2,3-dimethyl-1,3-butadiene in place of 2-methyl-2-pentene or 2-methyl-2-hexene. GC–MS analysis was performed on a diethyl ether extract of the crude reaction product, but preparative column chromatography was not performed.

3. Results and discussion

The allylic amination/C–C double-bond transposition reaction is shown below in Fig. 4, with yields for both alkenes and catalysts examined. While the analogous reaction performed by Nicholas and coworkers, using $[\text{Fe}(\text{az})_3](\text{FeCl}_4)_2$ as catalyst, used 1,4-dioxane as solvent [23,24], we found that better yields were obtained using acetonitrile.

The above results show that both Co complexes are effective catalysts for the amination of 2-methyl-2-pentene, each giving about 4 turnovers, but are much less effective for the amination of 2-methyl-2-hexene, with turnover numbers between 1 and 2. Nicholas and coworkers' work with $[\text{Fe}(\text{az})_3](\text{FeCl}_4)_2$ as catalyst yielded about 8.8 turnovers with 2-methyl-2-pentene as reactant, though this was based on a yield obtained from GC analysis, not an isolated yield. While Nicholas and coworkers did not report a yield for the amination of 2-methyl-2-hexene catalyzed by $[\text{Fe}(\text{az})_3](\text{FeCl}_4)_2$ directly, they did obtain about 5 turnovers for that reaction when a 9:1 mixture of FeCl_2 and FeCl_3 were used as precatalyst, presumably generating $[\text{Fe}(\text{az})_3]^{2+}$ in situ [24].

We propose that one factor limiting catalytic efficiency may be the deoxygenation of PhNO or its azodioxide dimer. GC–MS analysis of a diethyl ether extract of the reaction mixtures showed both azobenzene, PhNNPh (m/z 182) and azoxybenzene, PhNN(O)Ph (m/z 198), which may be formed by oxygenation of the Co catalysts to yield catalytically inactive species. Nicholas and coworkers also observed the formation of azobenzene and azoxybenzene in their reaction mixtures [24], and this side reaction may be more significant in our cobalt-catalyzed reactions.

To determine whether an on-metal or an off-metal mechanism was operative, we performed trapping experiments in which $[\text{Co}(\text{az})_4](\text{PF}_6)_2$ or $[\text{Co}(\text{bpy})(\text{az})_2](\text{PF}_6)_2$ was treated with 2,3-dimethyl-1,3-butadiene (DMB) in place of a monoalkene, in the absence of PhNHOH. As shown in Fig. 5 below, these reactions yielded no allylic amination product of DMB, but did produce the Diels-Alder cycloadduct of DMB and PhNO

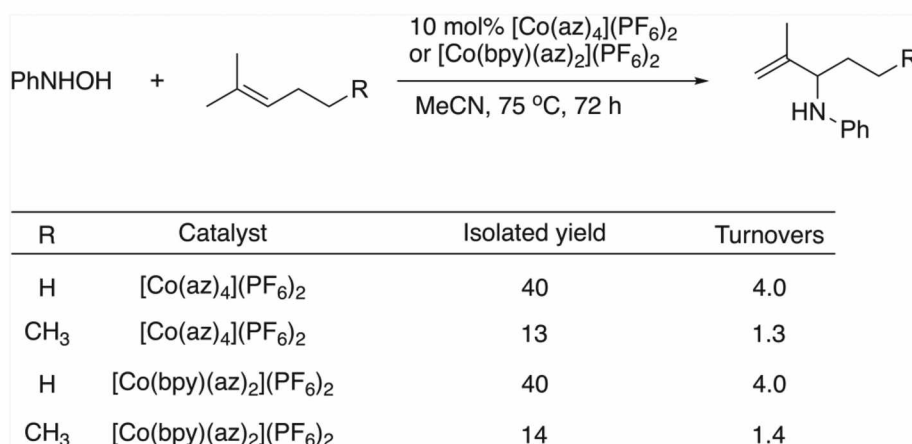


Fig. 4. Cobalt-catalyzed allylic amination/C–C double-bond transposition.



Fig. 5. Diels-Alder trapping experiments with 2,3-dimethyl-1,3-butadiene.

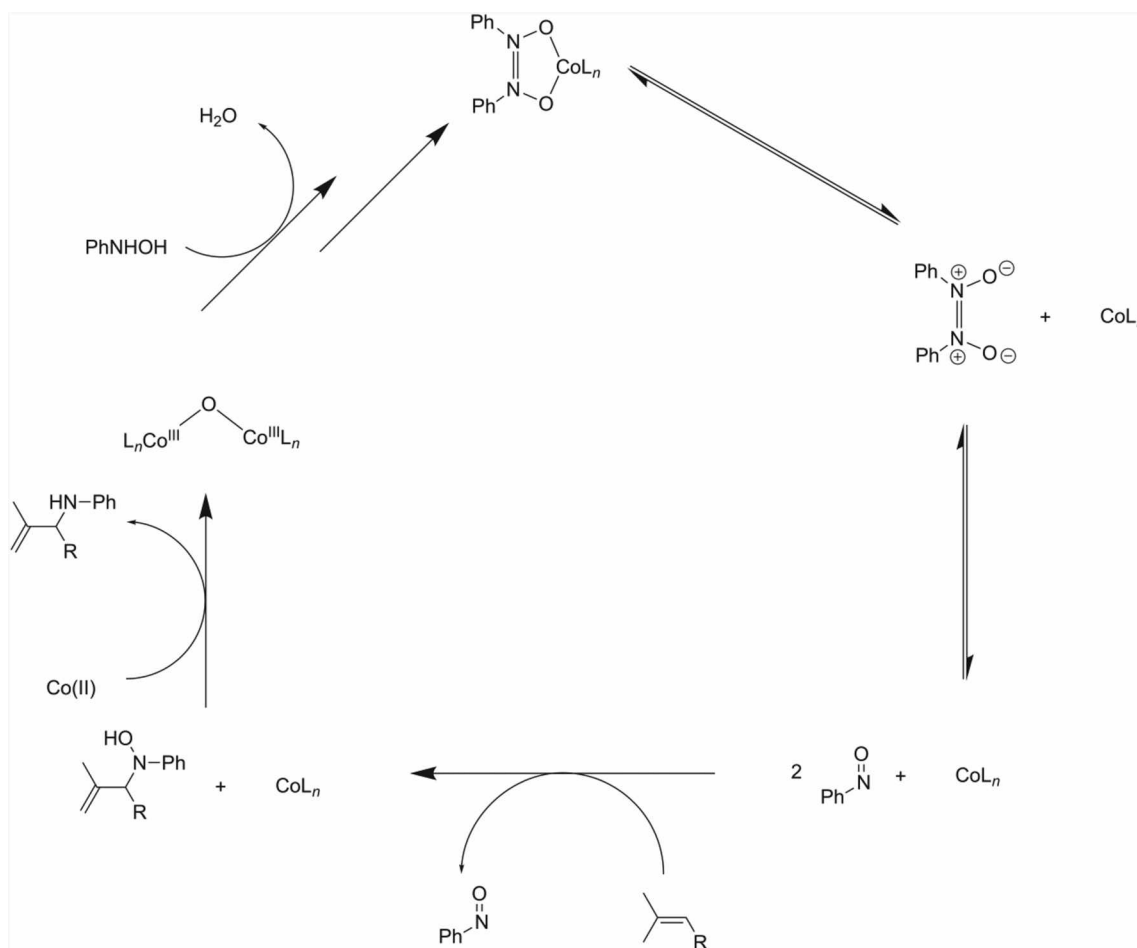


Fig. 6. Proposed partial mechanism for cobalt(II) azodioxide complex-catalyzed amination.

(m/z 189), as observed by GC-MS analysis of a diethyl ether extract of the reaction mixture.

The formation of the DMB/PhNO cycloadduct suggests the formation of free PhNO as the active aminating agent in the catalytic reactions. This result indicates that the reactions proceed by an off-metal process that contrasts strongly with the on-metal process observed by Nicholas and coworkers for reactions catalyzed by $[\text{Fe}(\text{az})_3](\text{FeCl}_4)_2$ [24], but which is reminiscent of the generation of free (2-MeOC₆H₄)NO observed by Whiting and coworkers with their Sc(III) complex [28]. We propose the partial mechanism shown in Fig. 6 below, in which free PhNO, generated from a dissociated azodioxide ligand, reacts with alkene to form a hydroxylamine, which is then converted to an amine with formation of a bimetallic Co(III) complex with a bridging oxido ligand. Finally, PhNHOH is dehydrogenated by this oxido complex, yielding water and regenerating PhNO. Such redox chemistry would not be plausible with azodioxide complexes containing redox-inactive metal centers such as Sc(III) [28] or Ca(II) [27], but is possible for Fe and Co complexes, as both the +2 and +3 oxidation states are readily accessible for each of these metals.

4. Conclusion

The cobalt(II) azodioxide complexes $[\text{Co}(\text{az})_4](\text{PF}_6)_2$ and $[\text{Co}(\text{bpy})(\text{az})_2](\text{PF}_6)_2$ have been shown to catalyze the allylic amination/C–C double bond transposition reaction of 2-methyl-2-pentene with phenylhydroxylamine, with the analogous reaction with 2-methyl-2-hexene proceeding with substantially lower efficiency. Diels-Alder trapping experiments suggest an “off-metal” mechanism involving the

generation of free nitrosobenzene. Such a mechanism is significantly different from the “on-metal” mechanism proposed by Nicholas and coworkers for allylic amination/C–C double bond transposition catalyzed by the iron(II) azodioxide complex salt $[\text{Fe}(\text{az})_3](\text{FeCl}_4)_2$ [24], and it indicates that “off-metal” mechanistic behavior is possible with the redox-active Co(II) center, as well as with the redox-inactive Sc(III) center in the complex of Whiting and coworkers [28]. Future work will focus on the preparation of modified cobalt catalysts to improve the yield and scope of this reaction, as well as to allow for the transient generation of unstable nitroso species such as acylnitroso compounds [33–35]. Additionally, we will explore the application of this amination technique to the synthesis of bioactive molecules.

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