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Catalytic Tetrazole Synthesis via [3+2] Cycloaddition of NaN$_3$ to Organonitriles Promoted by Co(II)-complex: Isolation and Characterization of a Co(II)-diazido Intermediate

Archana Babu and Arup Sinha*

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ABSTRACT: The [3+2] cycloaddition of sodium azide to nitriles to give 5-substituted 1H-tetrazoles is efficiently catalyzed by a Cobalt(II) complex (**1**) with a tetradentate ligand *N,N*-bis(pyridin-2-ylmethyl)quinolin-8-amine. Detailed mechanistic investigation shows the intermediacy of the cobalt(II) diazido complex (**2**), which has been isolated and structurally characterized. Complex **2** also shows good catalytic activity for the synthesis of 5-substituted 1H-tetrazoles. These are the first examples of cobalt complexes used for the [3+2] cycloaddition reaction for the synthesis of 1H-tetrazoles under homogeneous conditions.

Cobalt(II)-diazido intermediate
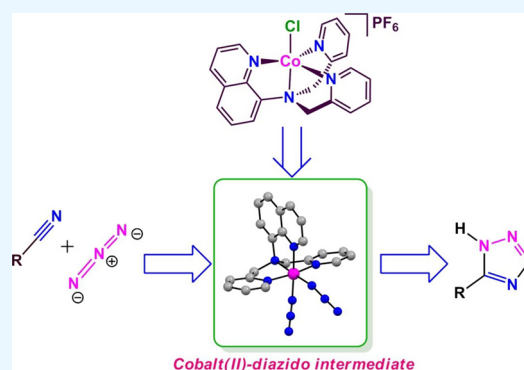
INTRODUCTION

Tetrazoles are the highest number of nitrogen atoms containing thermally stable heterocyclic compounds. These unnatural heterocyclic compounds have largely manifested their applications in medicinal chemistry and pharmaceutical science.[1–8] Due to the longer biodisponibility, the tetrazole moiety increases the activity of the drug without affecting the active pharmaceutical ingredient. Furthermore, the acidic nature of 5-substituted 1H-tetrazoles renders them to act as bioisosteric replacements of carboxylic acids.[9–11] A large variety of tetrazole fragments containing drug molecules have been reported to date.[12–14] Due to their high energy properties, tetrazole derivatives also found their applications as potential explosives and in the manufacturing of high-energy materials.[15–20] Furthermore, tetrazole derivatives are used for the preparation of ligands for various kinds of coordination complexes.[21–25] These nitrogen-rich heterocyclic compounds are also extensively used as effective organocatalysts.[26–30]

With growing interest toward the development of novel tetrazole derivatives, several synthetic methods have evolved.[31–34] In particular, the [3+2] cycloaddition of azide with organic nitrile has been the most proficient route to 5-substituted 1H-tetrazoles.[35–37] To minimize the high activation barrier associated with the cycloaddition reactions, several homogeneous[38–41] and heterogeneous[42–46] catalysts and additives have been used. Many of those involve the use of expensive and toxic metals,[47–51] strong Lewis acids,[52–56] and mediated via highly explosive and toxic hydrazoic acid.[57,58] Although transition metal salts have been widely used to catalyze the synthesis of 5-substituted 1H-tetrazoles via dipolar

cycloaddition,[59–66] use of metal complex catalysts is relatively limited.[67] Bharathi and co-workers have developed a series of ruthenium(II) (η^6-p-cymene) complexes, which are capable of catalyzing three-component syntheses of 2,4,5-5-substituted 1H-tetrazole derivatives.[68] El-Remaily used Fe(III)-porphyrin complex (5,10,15,20-tetrakis(4-sulfonatophenyl)-porphyrin-iron(III)chloride (FeTSPP) to effect the [3+2] cycloaddition in aqueous medium for the synthesis of fluorinated guanindinyl tetrazole derivatives.[69] Chanda and Maiti reported the usefulness of the $[Cu(phen)(PPh_3)_2][NO_3]$ complex for [3+2] cycloaddition of azide with organic nitriles under homogeneous conditions.[70] Pathak[71,72] and Ghosh[73] have independently demonstrated the utility of Cu(II)-Schiff base and Cu(II)-salen type complexes in catalyzing the synthesis of tetrazoles. Recently Kozakiewicz-Piekarz and co-workers have delineated the synthesis of 5-phenyl-1H-tetrazole from the reaction of benzonitrile and sodium azide using phenolato-bridged two dinuclear Zn(II) complexes carrying azido groups coordinated to each zinc ion.[74] To date, these are the only azido group containing complexes used to catalyze the synthesis of tetrazole. Although the catalytic utility of these complexes is limited by only one substrate and versatility of the
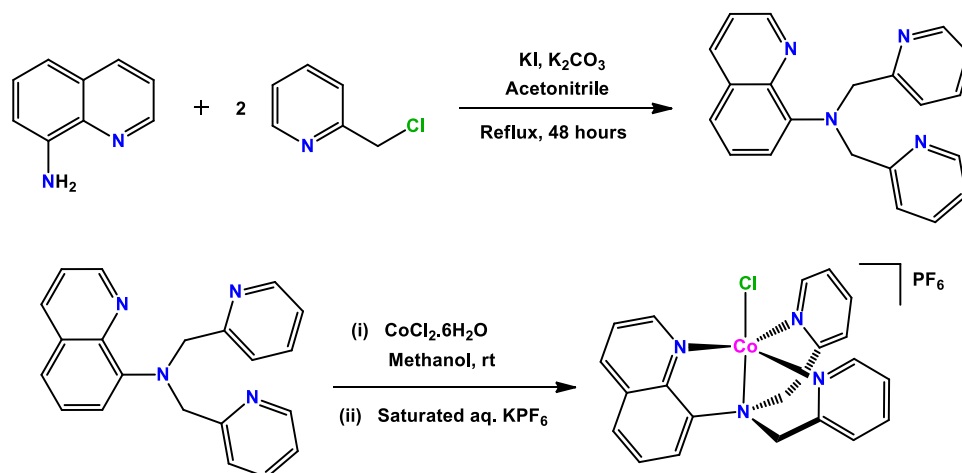
Scheme 1. Synthesis of *N,N*-Bis(pyridin-2-ylmethyl)quinolin-8-amine (L¹) and Complex 1

catalysts was not demonstrated. Mechanistically it is well established that azide directly interacts with nitrile attached to the metal catalyst. Therefore, it is expected that azide ligand coordinated to the metal center can offer better activity in the cycloaddition step. Indeed, the dinucelar Zn(II) complexes catalyzed the [3+2] cycloaddition at a relatively lower temperature. Hence, it is imperative to use azido ligand-containing catalysts for better catalytic efficiency.

Over the past few decades, cobalt complexes have emerged as perfect replacements for the highly effective Platinum Group Metal (PGM) based catalysts. Flexible coordination geometries, tunable electronic states, and inherent lability render the cobalt complexes appropriate alternatives of PGM-based catalysts, which suffer from sustainability and environmental issues. A large variety of reactions, such as water oxidation, hydrogenation, hydroformylation, hydrosilylation, cross-coupling, C−H activation, and cycloaddition reactions, have been successfully catalyzed by a multitude of cobalt complexes with immaculate efficiency.[75−84] Despite being efficient catalytic systems in synthetic chemistry and transition metal catalysis, to date no cobalt complex has been used for the synthesis of 5-substituted 1H-tetrazoles via [3+2] cycloaddition under homogeneous conditions.

In this contribution, we report the first-time utilization of cobalt(II) complexes carrying a tetradentate ligand *N,N*-bis(pyridin-2-ylmethyl)quinolin-8-amine[85] for catalyzing the synthesis of 5-substituted 1H-tetrazoles via [3+2] cyclo-addition of NaN₃ to organonitrlecompounds. Furthermore, we also demonstrate the intermediacy of a novel structurally characterized cobalt(II) diazido complex during the synthesis of 5-substituted 1H-tetrazoles via [3+2] cycloaddition. To the best of our knowledge, this is the first time any intermediate has been structurally characterized during the [3+2] cyclo-addition of NaN₃ to organonitriles.

RESULTS AND DISCUSSION

Synthesis and Characterization of Ligand (L¹) and the Cobalt Complex (1).
The tetradentate ligand *N,N*-bis-(pyridin-2-ylmethyl)quinolin-8-amine (L¹) was synthesized by refluxing a stoichiometric mixture of 8-amino quinoline and 2-chloro-methylpyridine hydrochloride in the presence of potassium carbonate and potassium iodide in acetonitrile over a period of 48 h (Scheme 1) with good yield.[85] The ligand was characterized using various spectroscopic techniques. The

UV−vis data for the ligand was recorded in acetonitrile solution ($\sim 5 \times 10^{-3}$ M) (Figure S2). The transition observed at 250 nm ($\varepsilon = 552$ M^{-1} cm^{-1}) is assigned to the ligand centered $\pi-\pi^*$ transitions, whereas the band at 339 nm ($\varepsilon = 152$ M^{-1} cm^{-1}) is due to the n−π^* transition occurring between the tertiary amine to the heteroaromatic ring. A characteristic band corresponding to the aromatic C−H stretching was observed in the range of 3137−2796 cm^{-1} in the IR spectra (Figure S3). The NMR spectra were recorded in dimethyl sulfoxide-d⁶ (DMSO-d⁶) (Figure S4). In the ¹H NMR spectrum, a four-proton singlet at δ 4.8 ppm is attributed to two methylene groups adjacent to the pyridyl moieties. Signals corresponding to the aromatic protons of quinoline and pyridyl group appear in the range of δ 6.9 to 8.7 ppm. In the ¹³C NMR spectrum, methylene carbons resonate at δ 59.16 ppm and the aromatic protons appear in the range of δ 159.60−117.68 ppm. electrospray ionization mass spectrometry (ESI-MS) data show the base peak signal at $m/z = 327.1615$ corresponding to $[C_{21}H_{18}N_4 + H]^+$ (Figure S6).

The cobalt complex **1** was synthesized in two steps (Scheme 1). First, the reaction of ligand L¹ with CoCl₂·6H₂O in a 1:1 molar ratio in methanol afforded the complex with chloride anion. In the second step this hygroscopic complex was subjected to the salt metathesis by adding a saturated aqueous KPF₆ solution to afford the brown colored complex **1** with hexafluorophosphate counteranion in good yield. Resulting complex was characterized by UV−vis and IR spectroscopy. The UV−vis spectrum of the complex **1** was recorded in acetonitrile solution ($\sim 5 \times 10^{-3}$ M) at room temperature (Figure S7).

In UV−vis spectra, a transition band was observed at 305 nm ($\varepsilon = 204$ M^{-1} cm^{-1}), which is due to ligand to metal centered $\pi-\pi^*$ transitions, and at 394 nm ($\varepsilon = 124$ M^{-1} cm^{-1}), which is assigned as the n−π^* transition between tertiary amine to heteroaromatic ring. In IR spectra, a strong band at 711 cm^{-1} indicates the presence of the hexafluor-ophosphate anion (Figure S8). The ESI-MS studies were recorded in acetonitrile solution in which the signal at $m/z = 420.047$ corresponds to $[C_{21}H_{18}N_4CoCl]^+$ and $m/z = 385.074$ corresponds to $[C_{21}H_{18}N_4Co]^+$ species (Figure S9).

Catalytic [3+2] Cycloaddition of NaN₃ to Organo-nitriles Catalyzed by Complex 1.
Initially, complex **1** was used to investigate its catalytic activity toward the synthesis of tetrazoles. In order to optimize the reaction conditions, we

Table 1. Effects Reaction Conditions for Catalytic Synthesis of 5-Substituted 1H-Tetrazoles via [3+2] Cycloaddition of NaN$_3$ to Organonitrle Compounds
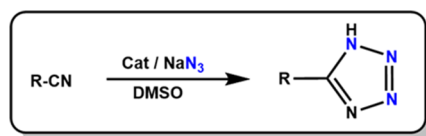
entry	catalyst	NaN$_3$ (equiv)	catalyst loading (mol %)	solvent	temperature (°C)	time (h)	yield (%)[a]
1	L^1	1.2		DMSO	110	24	0
2	CoCl$_2$	1.2	0.5	DMSO	110	24	0
3	L^1 + CoCl$_2$	1.2	0.5	DMSO	110	12	0
4	**1**	1.2	0.5	DMSO	110	12	78
5	**1**	1.2	0.5	DMSO	110	24	40
6	**1**	1.2	1	DMSO	110	24	80
7	**1**	1.2	1	DMSO	110	12	99
8	**1**	1.2	1	Methanol	110	12	20
9	**1**	1.2	1	Toluene	110	12	15
10	**1**	1.2	1	ACN	110	12	50
11	**1**	1.2	1	DMF	110	12	80
12	**2**	1.2	0.5	DMSO	110	12	75
13	**2**	1.2	0.5	DMSO	110	24	48
14	**2**	1.2	1	DMSO	110	12	85
15	**2**	1.2	1	DMSO	110	24	60

[a]Isolated yield after column chromatography; DMSO = dimethyl sulfoxide; ACN = acetonitrile; DMF = N,N-dimethylformamide.

Scheme 2. Complex 1 Catalyzed Synthesis of 5-Substituted 1H-Tetrazoles via [3+2] Cycloaddition of NaN$_3$ to Organonitrle Compounds[a]
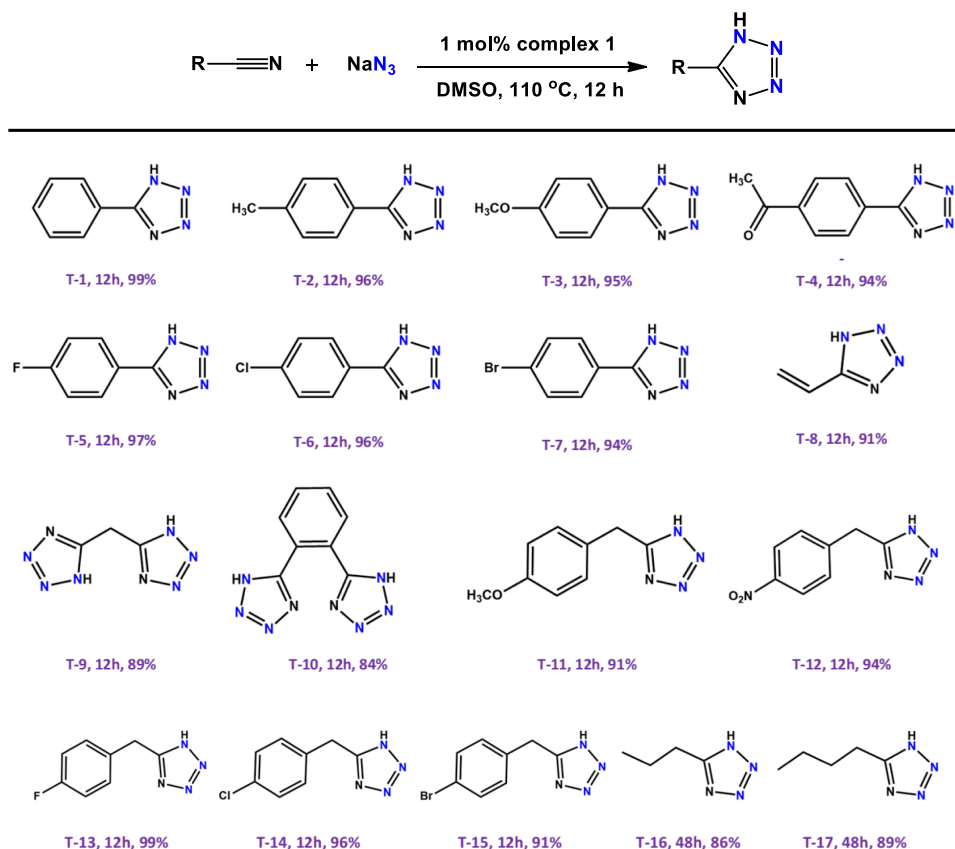

[a]Reported yields are isolated yields after purification by column chromatography.

have reacted benzonitrile as a model substrate with sodium azide in the presence of a catalytic amount of complex **1**. Various parameters were optimized and measured such as time, catalyst loading, azide loading, and solvents. The results are summarized in Table 1. First, we did solvent optimization using 1 mol % catalyst and 1.2 equiv of sodium azide at 110

Scheme 3. Synthesis of the Co(II)-diazido Complex (2)
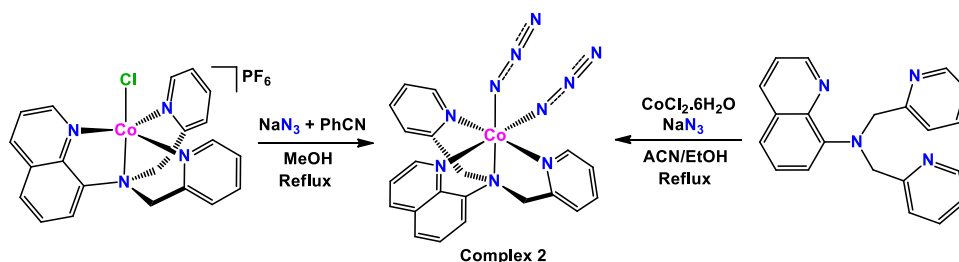
°C. The reaction was performed for 12 h in various solvents such as DMSO, methanol, toluene, acetonitrile, and dimethylformamide (Table 1, Entries 7, 8, 9, 10, and 11). Methanol and toluene were found to be inefficient with meager yields of 20 and 15%, respectively. The product yield significantly increased to 50% in acetonitrile, and the yield further increased to 80% in dimethylformamide (DMF). With an excellent yield of 99%, DMSO was found to be the best solvent for the tetrazole synthesis catalyzed by the 1. No product formation was observed when the reaction was performed in the absence of complex 1, even for prolonged reaction time (Table 1, Entries 1, 2, and 3). Product yield got reduced to 78% when we lowered the catalyst load to 0.5 mol % while performing the reaction under the reaction conditions mentioned in Table 1, Entry 4. The product yield further decreased to 40% when the reaction was performed for a longer time (Table 1, Entry 5). Reduced yield might be due to the partial thermal decomposition of tetrazole on prolonged heating at the given temperature.[86,87] Similar reduction of yield was observed whenever the reaction was performed for a longer time (Table 1, Entries 6, 13, and 15). Therefore, the effect of time was also optimized, and the best product formation was achieved with maximum yield at 12 h. Therefore, 1 mol % catalyst loading to the substrate for 12 h was found to be optimum (Table 1, Entry 7).

After optimizing all the reaction parameters, the reaction was explored on a variety of organonitrile compounds. Both aromatic and aliphatic nitrile substrates were subjected to the optimized catalytic conditions. The nitrile substrates were heated at 110 °C in DMSO for 12 h with 1.2 equiv of NaN$_3$ in the presence of 1 mol % of complex 1. The results are summarized in Scheme 2. All aromatic nitriles afforded the corresponding tetrazoles (T1−T7) with excellent yields. Functional groups had a negligible effect on the product yields. Vinyl tetrazole (T8) was obtained from acrylonitrile in good yield without affecting the double bond. Product yield got diminished to below 90% for malononitrile and phthalonitrile. Corresponding bis-tetrazole derivatives (T9 and T10) were obtained in 89 and 84% yields, respectively. The yield was reduced due to the adjacent positions (1,1 for malononitrile and 1,2 for phthalonitrile) of two cyano groups. Benzyl nitrile derivatives afforded respective tetrazole derivatives (T11−T15) in very good yields. Longer reaction times (48 h) were required for butyronitrile and valeronitrile to get a good product yield of 86 (T16) and 89% (T17).

Mechanistic Investigation of the Co-catalyzed [3+2] Cycloaddition of NaN$_3$ to Organonitriles. The synthesis of tetrazole involves the [3+2] cycloaddition of nitrile with azide. It has been proposed that the metal-catalyzed reaction involves the initial coordination of either azide or the nitrile to the metal center.[88] In order to elucidate the mechanism of the

tetrazole formation reaction, we set to perform a series of control reactions as shown in Scheme 3. To predict the initial coordination of azide, we treated the parent complex 1 with sodium azide and benzonitrile in methanol under reflux. An intermediate cobalt diazido complex 2 was isolated and structurally characterized. The complex 2 was also synthesized by refluxing a mixture of L^1 with CoCl$_2$ in the presence of two equivalents of NaN$_3$ in a mixed solvent of methanol and acetonitrile. The red complex 2 crystallized in the $P\bar{1}$ space group.

The molecular structure of 2, as presented in Figure 1, shows a pseudo-octahedral complex where four coordination
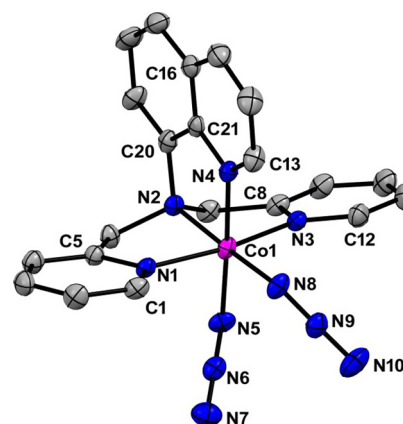

Figure 1. Molecular structure of the cationic unit of complex 2, where thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (deg) are listed in Table 3.

sites of the central cobalt atom are occupied by four nitrogen atoms from two pyridyl (N1 and N3), one quinolyl (N4), and one tertiary amine (N2) groups of the ligand. The remaining two sites are coordinated by two azido nitrogen atoms (N5 and N8). The cobalt-heteroaromatic N distances (Co1−N1 or N3 or N4) fall in the range of 1.931(4)−1.941(4) Å. Due to weak ligand strength cobalt-tertiary amine nitrogen bond (Co1−N2) length is slightly longer than other Co-heteroaromatic N (1.970(3) Å). Interestingly all the Co-ligand bonds are significantly shorter than the bond lengths reported for the cobalt(II) complexes carrying polypyridyl tetradentate ligands.[89] The two linear azide ligands (∠N−N−N angles 175.9(5)° and 176.9(5)°) are cis to each other and bind the cobalt ion in a bent fashion with ∠Co1−N5−N6 and ∠Co1−N8−N9 being 115.6(3)° and 122.2(3)°, respectively. The Co-azide bond trans to the quinolyl nitrogen is shorter compared to the bond trans to the tertiary amine nitrogen of the ligand (Co1−N8 = 1.925(4) Å and Co1−N5 = 1.941(4) Å). Interestingly, for both azide ligands, the N−N bond lengths

within the ligand are unequal. The "N−N−N" bond parameters are similar to those found in N_3H.[90] The N5−N6 and N8−N9 bond distances (1.200(6) and 1.203(6) Å) are longer than those of the N6−N7 and N9−N10 bonds (1.151(6) and 1.145(6) Å). This indicates that the proximal N−N bonds are intermediate between single and double bonds, whereas the distal N−N bonds are intermediate between double and triple bonds.[89]

Complex **2** was further characterized by spectroscopic techniques. The UV−vis spectra of the complex were recorded in acetonitrile solution ($\sim 5 \times 10^{-3}$ M) at room temperature, and the corresponding spectra are presented in Figure S10, which shows the ligand centered $\pi-\pi^*$ transition at 312 nm (ε = 318 M^{-1} cm^{-1}). On the other hand, the transition band at 408 nm (ε = 165.63 M^{-1} cm^{-1}) is assigned to the d−d transition in pseudo-octahedral environment. In the IR spectra (Figure S11), a sharp characteristic band for azide was observed around 2006 cm^{-1}. Two major signals at mass-to-charge ratios (m/z) of 428.0983 and 471.1206 were observed in the ESI-MS (Figure S12). These signals are attributed to $[L^1Co(N_3) + H]^+$ and $[L^1Co(N_3)_2 + 2H]^+$ fragments, indicating a facile Co-azide ligand dissociation process, which is a crucial step during the catalysis reaction.

In order to gather more evidence for the intermediacy of the diazido complex **2**, we performed the tetrazole synthesis by reacting nitrile compounds with 1.2 equiv of NaN_3 in the presence of the catalytic amount of complex **2** (Table 1, Entries 7, 8, 9, 10, and 11). The formation of tetrazole in a good yield clearly shows the intermediacy of the bisazido complex.

To get further insights, the complex **2** was treated with one equivalent of benzonitrile (Scheme 4) and the reaction was

Scheme 4. Reaction of Complex 2 with Benzonitrile
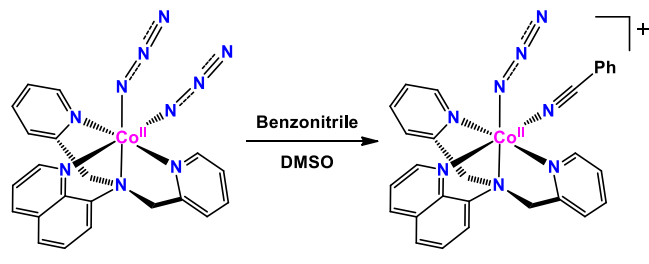
monitored by IR spectroscopy for 12 h (Figure 2). We observed that with the progress of the reaction the intensity of
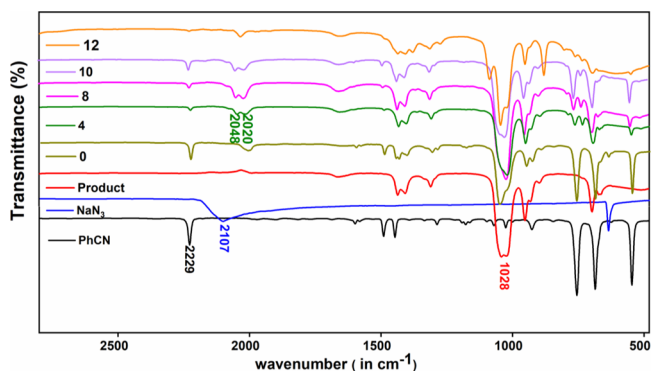

Figure 2. Monitoring the progress of the reaction of Complex **2** with benzonitrile.

the C≡N stretching frequency at 2229 cm^{-1} starts to decrease with the concomitant appearance of two new bands at 2048 and 2020 cm^{-1}, which clearly indicates the coordination of nitrile to the cobalt metal center. It is well-known that the value of C≡N stretching vibration decreases upon coordination to the metal center. Band at 2048 cm^{-1} is assigned to the coordinated nitrile and 2020 cm^{-1} is due to the coordinated azido ligand. This indicated the intermediacy of the $[L^1Co-(N_3)(N≡C-Ph)]^+$ species. The intermediacy of the $[L^1Co-(N_3)(N≡C-Ph)]^+$ species has been proven further when the reaction was performed in the presence of two equiv of benzonitrile; exactly the same IR pattern was obtained as we got for reaction with one equivalent of benzonitrile. No evidence for the formation of the $[L^1Co(N≡C-Ph)_2]^{2+}$ species was found. Based on the above-mentioned controlled reactions, we propose the catalytic cycle for the formation of tetrazole in Scheme 5.

Scheme 5. Proposed Mechanistic Cycle for the Co-catalyzed [3+2] Cycloaddition of NaN_3 to Organonitriles
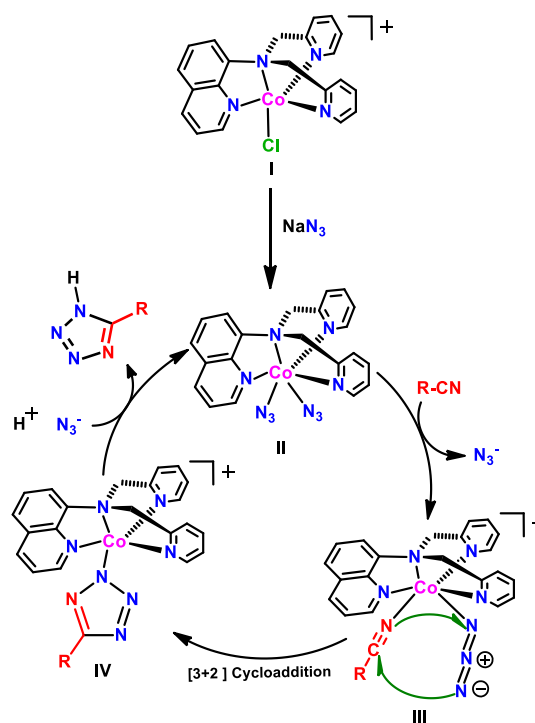
Initially the Co-diazido intermediate species **II** (complex **2**) is generated via the reaction of the Co−Cl complex (**I**) with NaN_3. In the second step, the nitrile substrate reacts with the active species **II** to generate the intermediate $[L^1Co(N_3)(N≡C-Ph)]^+$ (**III**), the presence of which was identified by IR spectroscopic studies. Coordinated azide and aryl nitrile then undergo the [3+2] cycloaddition to form the desired tetrazole, which then gets expelled from the cobalt center via the coordination of two azide ligands to get the active intermediate species **II**, which subsequently re-enters the catalytic cycle.

■ SUMMARY AND CONCLUSIONS

In summary, we have developed a new cobalt(II) complex **1** carrying a tetradentate ligand system. The complex has shown excellent activity toward the synthesis of 1H-tetrazoles via [3+2]-cycloaddition of azide to aryl nitrile under mild reaction

conditions. This is the first report where cobalt complexes are used for 1H-tetrazole synthesis via click chemistry under homogeneous conditions. Near quantitative yields were obtained for majority of substrates. Detailed mechanistic studies have been performed to get clear understanding about the mechanism. This shows the intermediacy of a cobalt(II) diazido species (**2**) which was isolated and structurally characterized by single-crystal X-ray diffraction (XRD). The isolated cobalt(II) diazido complex has also demonstrated good catalytic activity.

■ EXPERIMENTAL SECTION

Materials and Methods. All chemicals were purchased from commercial suppliers and used without further purification. Solvents used for the reactions were purified by distillation. Deuterated solvents used for spectroscopic studies were purchased from Sigma-Aldrich. Thin-layer chromatography (TLC) used for reaction monitoring was developed on Merck 1.05554 aluminum sheets precoated with silica gel 60 F254. Spots were visualized under UV light at 254 nm or under iodine. Column chromatography was performed on a silica gel (60−120 mesh) static phase.

Instrumentation. All NMR spectra were recorded using a Bruker Avance III 400 MHz spectrometer. Chemical shifts (δ) are denoted in ppm using the residual proton resonance of the solvent as an internal standard (CHCl3: δ = 7.26 ppm for ^{1}H spectra, 77.2 ppm for ^{13}C{1H} spectra; (CD$_3$)$_2$SO: δ = 2.50 ppm for 1H spectra, 39.7 ppm for ^{13}C{1H} spectra). ESI mass data were obtained from a WATERS−XEVO G2-XS-QToF high-resolution mass spectrometer. IR and UV−vis spectra were recorded on Thermo-Scientific Nicolet iS50 and Agilent Cary 60 spectrophotometers, respectively.

X-ray Crystallography. X-ray data were collected on a FIXED-CHI four-axis goniometer, Bruker AXS D8 Quest diffractometer, equipped with a PHOTON II detector. Data collections were performed at 300 K using a monochromatized MoKα (λ = 0.71073 Å) X-ray radiation from IμS 3.0 microfocus X-ray sources. Indexing, integration, and scaling were performed with the Bruker SAINT embedded in APEX4 software package.[91] Absorption corrections were performed using the SADABS[92] implanted in APEX4. The structure solution and refinement were done by using the SHELX[93] suite of programs in the OLEX2-1.5[94] software package. Structure refinement was carried out by least-squares methods on weighted F2 values. The "riding method" was used to fix the hydrogen atoms.[95] Images of the molecular structures were created by the Mercury 4.0 program.[96] The solvent mask, which is the "SQUEEZE"[97] equivalent in the OLEX2-1.5 program, was used to remove a disordered solvent molecule from the overall intensity data for complex **2**. Important data collection and structure solution parameters are listed in Table 2.

Synthesis of (N,N-bis pyridin-2-yl methyl) Quinolin-8-amine (L^1). The ligand was synthesized according to the previously reported method.[85] A mixture of 2-chloromethylpyridine hydrochloride (104 mmol, 1.70 g), 8-aminoquinoline (0.34 mmol, 0.50g), potassium carbonate (104 mmol, 1.43 g), and potassium iodide (104 mmol, 1.72 g) were dissolved in acetonitrile (80 mL) and was heated at reflux for 48 h. The solution was cooled to room temperature, and then the solvent was evaporated, and the residue was extracted with acetate. The organic phase was evaporated and dried in a vacuum. The product was further purified by silica gel

Table 2. Crystallographic Data and Pertinent Refinement Parameters for Complex 2

empirical formula	C$_{21}$H$_{18}$N$_{10}$Co
formula weight	469.104
temperature/K	300.0
crystal system	triclinic
space group	P$\bar{1}$
a/Å	8.8887(14)
b/Å	11.0185(16)
c/Å	13.332(2)
α/°	97.724(7)
β/°	111.944(6)
γ/°	1182.7(3)
volume/Å^3	1182.7(3)
Z	2
ρ_{calc} g/cm^3	1.318
μ/mm^{-1}	0.754
F(000)	482.0
crystal size/mm^3	0.35 × 0.17 × 0.08
radiation	MoKα (λ = 0.71073)
2Θ range for data collection	4.058 to 52.942
reflections collected	28290
independent reflections	4772 [R_{int} = 0.0850, R_{sigma} = 0.0852]
data/restraints/parameters	4772/0/289
goodness-of-fit on F2	1.080
final R indexes [I ≥ 2σ (I)]	R1 = 0.0849, wR2 = 0.1537
final R indexes [all data]	R1 = 0.1214, wR2 = 0.1687

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complex 2

bond length (Å)	
Co1−N1	1.931(4)
Co1−N2	1.970(3)
Co1−N3	1.941(4)
Co1−N4	1.936(4)
Co1−N5	1.941(4)
Co1−N8	1.925(4)
N5−N6	1.200(6)
N6−N7	1.151(6)
N8−N9	1.203(6)
N9−N10	1.145(6)
bond angle (deg)	
N1−Co1−N2	84.57(15)
N1−Co1−N3	167.98(15)
N1−Co1−N4	89.65(16)
N1−Co1−N5	90.13(17)
N1−Co1−N8	95.32(17)
N2−Co1−N3	83.46(15)
N2−Co1−N4	86.53(16)
N2−Co1−N5	89.96(16)
N2−Co1−N8	117.11(18)
N3−Co1−N4	90.66(16)
N3−Co1−N5	88.83(17)
N3−Co1−N8	96.69(17)
N4−Co1−N5	176.50(16)
N5−Co1−N8	92.92(18)
N5−N6−N7	176.95(5)
N8−N9−N10	175.6(5)
Co1−N5- N6	115.6(3)
Co1−N8 N9	122.2(3)

chromatography using petroleum ether and ethyl acetate as an eluent to obtain a reddish-brown viscous oil. Yield: 0.29 g (89%). **¹H NMR (400 MHz, DMSO-d₆):** δ 8.79−8.77 (dd, 1H), 8.44−8.41 (d, 2H), 8.0−7.9 (dd, 1H), 7.45−7.41 (dd, 4H), 7.31−7.30 (m, 3H), 7.04−7.01 (m, 2H), 6.95−6.92 (dd, 1H), 4.8 (s, 4H). **¹³C NMR (101 MHz, DMSO-d₆):** δ 159.60, 149.17, 148.09, 146.49, 142.42, 137.06, 137, 129.93, 126.89, 122.53, 122.45, 121.67, 120.73, 117.68, 59.16. **IR data (KBr, ν/cm⁻¹):** 3014, 2906, 1590, 1423, 1079, 732. **UV−vis [CH₃CN, λ_{max}/nm (ε/M⁻¹ cm⁻¹)]:** 250 nm (ε = 552 M⁻¹ cm⁻¹), 339 nm (ε = 152 M⁻¹ cm⁻¹). **ESI-MS (CH₃CN):** m/z calculated for $[C_{21}H_{18}N_4 + H]^+$: 327.1609, found 327.1615.

Synthesis of [L¹CoCl][PF₆] (1). A solution of ligand L¹ (0.20 mmol, 46.4 mg) in MeOH (5 mL) was added dropwise to a vigorously stirring mixture of CoCl₂.6H₂O (0.10 mmol, 23.8 mg). The resulting mixture was stirred at room temperature for 12 h to get a reddish-brown solution. Solvent was removed under a reduced pressure. The residue was dissolved in water and saturated aqueous KPF₆ solution was added to induce precipitation. The precipitate was collected by filtration, washed thoroughly with diethyl ether, and dried under vacuum to get a dark-brown color solid. Yield: 0.353 g (84%). **IR data (KBr, ν/cm⁻¹):** 2826, 2624, 2241, 2161, 1234, 1129, 711. **UV−vis [CH₃CN, λ_{max}/nm (ε/M⁻¹cm⁻¹)]:** 305 nm (ε = 204 M⁻¹ cm⁻¹), 394 nm (ε = 124 M⁻¹ cm⁻¹). **ESI-MS (CH₃CN):** m/z calculated for $[C_{21}H_{18}N_4CoCl]^+$: 420.0552, found 420.0476; m/z calculated for $[C_{21}H_{18}N_4Co]^+$: 385.0863, found 385.0743.

Synthesis of [L¹Co(N₃)₂] (2). A solution of ligand (0.20 mmol, 46.4 mg) in EtOH (5 mL) was added dropwise to a vigorously stirring solution of CoCl₂·6H₂O (0.10 mmol, 23.8 mg) and NaN₃ (0.20 mmol, 13.0 mg) in a mixture of EtOH (5 mL) and CH₃CN (10 mL). The reaction mixture was stirred under reflux for 15 min and filtered. Diethyl ether was added to the filtrate to induce precipitation, which was filtered through the Whatman filter paper. The precipitate was further washed with diethyl ether, which was dried under vacuum to get a brownish-red color solid. Red color crystals were obtained by slow vapor diffusion of diethyl ether into acetonitrile solution at 0 °C and were used for structure determination by single-crystal XRD. Yield: 0.331 g (78%). **IR data (KBr, ν/cm⁻¹):** 3336, 2006, 1635, 1589, 1393, 1270, 755. **UV−vis [CH₃CN, λ_{max}/nm (ε/M⁻¹cm⁻¹)]:** 312 nm (ε = 318 M⁻¹cm⁻¹), 408 nm (ε = 165.63 M⁻¹cm⁻¹). **ESI-MS (CH₃CN):** m/z calculated for $[C_{21}H_{18}N_4Co(N_3) + H]^+$: 428.1034, found 428.0983 and for $[C_{21}H_{18}N_4Co(N_3)_2 + 2H]^+$: 471.1204, found 471.1206.

Reaction of Complex 2 with Benzonitrile. A 25 mL round-bottom flask containing 1.0 mmol of nitrile and Complex **2** (1.0 mol %) in DMSO (6 mL) was added. The reaction was monitored by ATR-IR spectrum at 4 h intervals.

General Procedure for the Synthesis of 5-Substituted-1H-tetrazoles via the [3+2] Cycloaddition Reaction. Complex **1** (1.0 mol %) in DMSO (6 mL) was added to nitrile (1.0 mmol) and was taken in a 25 mL round-bottom flask. After stirring for 12 h at 110 °C, the progress of the reaction was monitored by TLC. After completion, the reaction was cooled to room temperature and the reaction mixture was treated with dilute HCl (1N, 10 mL) and then extracted with ethyl acetate (3 × 10 mL). The resultant organic layer was separated, washed with water, and dried over anhydrous Na₂SO₄. The solvent of the extract was removed under reduced pressure with a rotary evaporator to obtain the product. The crude products were purified by column

chromatography on silica gel using petroleum ether/ethyl acetate as an eluent. The isolated products were authenticated with ¹H and ¹³C NMR spectra, which are given in Supporting Information.

5-Phenyl-1H-tetrazole (T1). Off white solid. Yield: 144.23 mg (99%). ¹H NMR (400 MHz, DMSO) δ 8.14−8.12 (m, 2H), 7.66−7.63 (m, 3H). ¹³C NMR (101 MHz, DMSO) δ 155.77, 131.70, 129.87, 127.46, 124.62.

5-(4-Methyl phenyl)-1H-tetrazole (T2). White solid. Yield: 153.43 mg (96%). ¹H NMR (400 MHz, DMSO) δ 8.15−7.95 (d, 2H), 7.53−7.33 (d, 3H), 2.32 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 155.51, 141.98, 130.38, 127.35, 121.18, 21.38.

5-(4-Methoxyphenyl)-1H-tetrazole (T3). Yellowish white solid. Yield: 167.19 mg (95%). ¹H NMR (400 MHz, DMSO) δ 7.93−7.91 (d, 2H), 7.10−7.08 (d, 2H), 3.78 (s, 2H). ¹³C NMR (101 MHz, DMSO) δ 161.91, 155.22, 129.08, 116.75, 55.86.

5-(4-Acetyl phenyl)-1H-tetrazole (T4). Yellowish white solid. Yield: 176.14 mg (94%). ¹H NMR (400 MHz, DMSO) δ 8.31−8.29 (d, 2H) 8.19−8.17 (d, 2H), 2.6 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 198.04, 155.45, 138.82, 129.54, 127.77, 27.31.

5-(4-Fluoro phenyl)-1H-tetrazole (T5). White solid. Yield: 158.88 mg (97%). ¹H NMR (400 MHz, DMSO) δ 7.419−7.415 (d, 2H), 7.37−7.35 (d, 2H). ¹³C NMR (101 MHz, DMSO) δ 167.97, 155.78, 134.33, 130.71, 129.03.

5-(4-Chlorophenyl)-1H-tetrazole (T6). Yellow solid. Yield: 174.27 mg (96%). ¹H NMR (400 MHz, DMSO) δ 8.03−8.01 (d, 2H), 7.62−7.60 (d, 2H). ¹³C NMR (101 MHz, DMSO) δ 155.34, 136.38, 129.91, 129.12, 123.55.

5-(4-Bromophenyl)-1H-tetrazole (T7). White solid. Yield: 211.32 mg (94%). ¹H NMR (400 MHz, DMSO) δ 7.82−7.80 (d, 2H), 7.60−7.5 (d, 2H). ¹³C NMR (101 MHz, DMSO) δ 155.58, 135.00, 132.29, 130.98, 129.03.

5-Vinyl-1H-tetrazole (T8). White solid. Yield: 87.05 mg (91%). ¹H NMR (400 MHz, DMSO) δ 2.99−2.65 (m, 2H), 4.61−4.57 (t, 1H), 2.99−2.65 (m, 2H). ¹³C NMR (101 MHz, DMSO) δ 144.47, 132.74, 117.90.

(Di-1H-tetrazole) methane (T9). White solid. Yield: 135.08 mg (89%). ¹H NMR (400 MHz, DMSO) δ 5.84 (S, 2H), 2.61 (s, 2H). ¹³C NMR (101 MHz, DMSO) δ 155.00, 14.27.

1,2-(Di-1H-tetrazol-5-yl) benzene (T10). White solid. Yield: 180.13 mg (84%). ¹H NMR (400 MHz, DMSO) δ 8.07−8.05 (dd, 2H), 7.8−7.605 7.78−7.76 (dd, 2H). ¹³C NMR (101 MHz, DMSO) δ 155.88, 135.40, 131.91, 130.17.

5-(4-Methoxybenzyl)-1H-tetrazole (T11). Yellowish white solid. Yield: 172.90 mg (91%). ¹H NMR (400 MHz, DMSO) δ 7.29−7.27 (d, 2H), 6.96−6.94 (d, 2H), 3.91 (s, 2H), 3.75 (s, 3H). ¹³C NMR (101 MHz, DMSO) δ 163.32, 158.71, 130.18, 114.55,114.55, 55.49, 28.41.

5-(4-Nitrobenzyl)-1H-tetrazole (T12). Yellow solid. Yield: 192.25 mg (94%). ¹H NMR (400 MHz, DMSO) δ 8.23−8.21(d, 2H), 7.64−7.61 (d, 2H), 4.24 (s, 2H). ¹³C NMR (101 MHz, DMSO) δ 167.57, 155.69, 132.40, 130.87, 129.03, 28.45.

5-(4-Fluorobenzyl)-1H-tetrazole (T13). White solid. Yield: 175.67 mg (99%). ¹H NMR (400 MHz, DMSO) δ 7.376−7.370 (d, 2H), 7.17−7.15 (d, 2H), 3.97(s, 2H). ¹³C NMR (101 MHz, DMSO) δ 166.92, 160.80, 130.57, 130.49, 116.00, 22.15.

5-(4-Chlorobenzyl)-1H-tetrazole (T14). White solid. Yield: 186.44 mg (96%). ¹H NMR (400 MHz, DMSO) δ 7.40−7.38 (d, 2H), 7.35−7.32 (d, 2H), 4.29(s, 2H). ¹³C NMR (101 MHz, DMSO) δ 167.20, 134.94, 132.31, 130.93, 128.99, 28.57.

5-(4-Bromobenzyl)-1H-tetrazole (T15). Yellowish white solid. Yield: 216.60 mg (91%). ^{1}H NMR (400 MHz, DMSO) δ 7.53−7.51 (d, 2H), 7.28−7.26 (d, 2H), 4.28 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 167.16, 135.58,131.95, 131.35, 120.75, 28.82.

(5-Propyl)-1H-tetrazole (T16). White solid. Yield: 95.87 mg (86%). ^{1}H NMR (400 MHz, DMSO) δ 3.03−2.99 (t, 2H), 1.86−1.80 (m, 2H), 0.95−0.91 (t, 3H). ^{13}C NMR (101 MHz, DMSO) δ 155.73, 24.24, 20.09, 12.49.

(5-Butyl)-1H-tetrazole (T17). White solid. Yield: 112.03 mg (89%). 1H NMR (400 MHz, DMSO) δ 3.02−2.98 (t, 2H), 1.80−1.72 (q, 2H), 1.36−1.27. (m, 2H), 0.86−0.82 (t, 3H). ^{13}C NMR (101 MHz, DMSO) δ 155.85, 28.67, 22.11, 21.07, 12.47.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c02567.

NMR spectra of ligand and all tetrazole products; HRMS, IR, and UV−vis spectra of ligand and metal complexes; and IR data of the control reactions (PDF)

Accession Codes

CCDC 2331927 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, U.K.; Fax: + 44 1223 336033).

AUTHOR INFORMATION

Corresponding Author

Arup Sinha − *Advanced Catalysis Facility, Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Vellore 632 006, India;* orcid.org/0000-0002-6910-2051; Email: arup.sinha@vit.ac.in

Author

Archana Babu − *Advanced Catalysis Facility, Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Vellore 632 006, India*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.4c02567

Author Contributions

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Notes

The authors declare no competing financial interest.

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