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Regioselective Synthesis of Multisubstituted Furans via Metalloradical Cyclization of Alkynes with α-Diazocarbonyls: Construction of Functionalized α-Oligofurans

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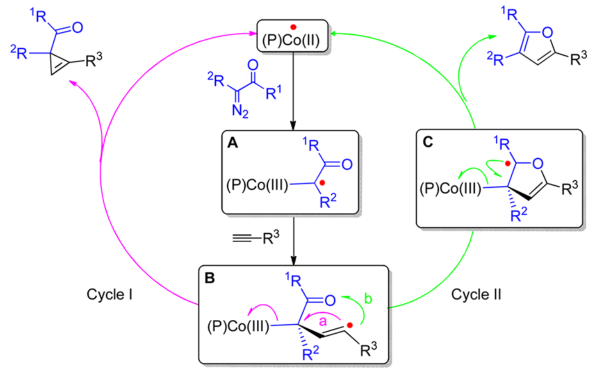
Supporting Information

ABSTRACT: Co(III)−carbene radicals generated from activation of α-diazocarbonyls by Co(II)−porphyrin complexes have been shown to undergo a new type of tandem radical addition reaction with alkynes that affords five-membered furan structures. The Co(II) complex of 3,5-Di^{t}Bu-IbuPhyrin, [Co(**P1**)], is effective in catalyzing the metalloradical cyclization reaction under neutral and mild conditions. The [Co(**P1**)]-catalyzed process tolerates a wide range of α-diazocarbonyls and terminal alkynes with varied steric and electronic properties, producing polyfunctionalized furans with complete regioselectivity. The catalytic synthesis features a high degree of functional group tolerance and can be applied iteratively to construct functionalized α-oligofurans.

Polyfunctionalized furans constitute an important class of five-membered O-heterocycles with widespread applications.[1] Their oligomers have also attracted considerable interest due to their great potential in material science.[2] Transition-metal-catalyzed cyclization reactions, especially intermolecular cyclizations of structurally simple starting materials, are among the most direct and practical methods for the construction of substituted furans.[3] Because of the synthetic ease of the substrates and the mild reaction conditions, such transformations have received increasing attention and have been recognized as some of the most appealing routes to polyfunctionalized furans.[3b−f,h−j] The Rh_2-catalyzed [3 + 2] cycloaddition of arylacetylenes with α-diazocarbonyl compounds represents one of the most direct approaches for the construction of polysubstituted furans.[4] Electron-rich arylacetylenes have been shown to form furans efficiently with different acceptor/acceptor (A/A)-substituted diazo reagents, as they tend to stabilize the key zwitterionic intermediate.[4b] Because they cannot provide this stabilization, other types of alkyne substrates, such as aliphatic and electron-deficient alkynes,[4b,5] generally perform poorly in the Rh_2-based furan synthesis, except when cyclic α-diazocarbonyls are used[6] or the reaction is carried out in an intramolecular fashion.[7] Moreover, direct access to furans with sensitive functionalities remains challenging in Rh_2- and other metal-based cycloaddition systems,[3,4b,8] which share common reaction mechanisms that are intrinsically ionic in nature. Evidently, there is a need to develop new catalytic systems for general and effective syntheses of polyfunctionalized furans from different alkynes and α-diazocarbonyls. To meet the remaining challenges in the field, it seems desirable to establish a fundamentally different catalytic system that operates in a nonionic manner.

Co(II)−porphyrin complexes [Co(Por)] with well-defined structures have emerged as unique metalloradical catalysts for olefin cyclopropanation.[9] Mechanistic studies have confirmed that Co(II)-based metalloradical cyclopropanation proceeds through an unusual Co(III)−carbene radical intermediate that undergoes stepwise radical addition−substitution.[10] A highly enantioselective cyclopropenation process was recently developed by applying the metalloradical catalysis to alkyne substrates (Scheme 1, cycle I).[11] To explore the use of metalloradical catalysis in other radical cyclization reactions, we envisioned the possibility of an alternative catalytic pathway leading to the construction of furans (Scheme 1, cycle II). In this process, the vinyl radical intermediate **B** generated from radical addition of Co(III)−carbene radical **A** to the alkyne would undergo a consecutive radical addition to the carbonyl group to give a new intermediate, **C**, which would release the furan product via radical β-scission. In addition to its fundamental importance, this catalytic tandem radical addition process would be synthetically attractive, as it would enable the direct synthesis of multisubstituted furans from α-diazocarbonyls and simple acetylenes. More importantly, its nonionic mechanism would enable a general furan synthesis with a high degree of functional group tolerance.

Scheme 1. Competitive Pathways for Co(II)-Based Metalloradical Cyclization of Alkynes with α-Diazocarbonyl Reagents: Cyclopropenation versus Furan Formation



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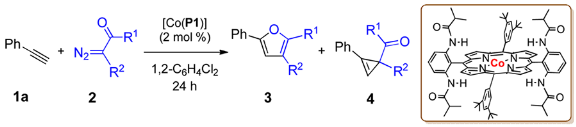
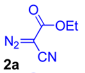
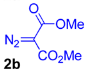
Herein we report a general and regioselective synthesis of polyfunctionalized furans involving intermolecular radical cyclization of acetylenes with A/A-substituted diazo reagents via Co(II)-based metalloradical catalysis. This unprecedented tandem addition pathway of Co(III)−carbene radicals has a broad substrate scope and can be applied to various combinations of α-diazocarbonyls and terminal acetylenes, including challenging aliphatic and electron-deficient alkynes. Furthermore, the metalloradical cyclization process can tolerate various functionalities (e.g., $-NR_2$, −CHO, and −OH).

Initial efforts investigated the possibility of [Co(Por)]-catalyzed furan formation from the reaction of phenylacetylene (**1a**) with α-cyanodiazoacetate **2a** (Table 1), which was previously shown to undergo cyclopropenation.[11] Using the Co(II) complex of the D_{2h}-symmetric amidoporphyrin 3,5-Di^{t}Bu-IbuPhyrin, [Co(**P1**)], as the catalyst,[12] we observed a significant dependence of the product distribution on the reaction temperature. While the reaction at room temperature produced cyclopropene **4aa** predominantly, 2,3,5-trisubstituted furan **3aa** was detected as the minor product and isolated in 31% yield (entry 1). To our delight, increasing the reaction temperature to 80 °C afforded **3aa** as the only regioisomer in 68% yield (entry 2). 2-Diazomalonates have commonly been used to prepare cyclopropene derivatives through Rh_2-catalyzed cyclopropenation of **1a**.[4b,13] Interestingly, although the reaction was slow at room temperature, 2-diazomalonate **2b** underwent effective [Co(**P1**)]-catalyzed cyclization with **1a** at 80 °C to form 2,3,5-trisubstituted furan **3ab** regioselectively in excellent yield with almost no cyclopropenation product (entries 3 and 4).[14] Further experiments showed that in the presence of [Co(**P1**)], **2a**/**2b**, and **1a** at 80 °C, the previously prepared cyclopropene **4aa**/**4ab** did not undergo effective isomerization to give the corresponding furan **3**, indicating that the furan is formed directly from cyclization of **1a** with the diazo reagent rather than from ring expansion of the initially formed cyclopropene.[15] These results clearly showed that the Co(II)-catalyzed cyclopropenation pathway can be completely switched to furan formation through judicious use of the diazo reagent at a higher reaction temperature (Scheme 1).

Table 1. Influence of the Diazo Reagent and Temperature on the Formation of Furans versus Cyclopropenes via [Co(P1)]-Catalyzed Cyclization with Phenylacetylene[a]

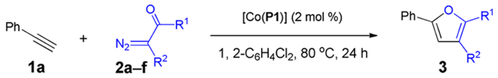


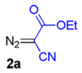
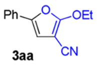
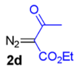
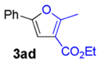
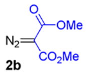
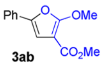
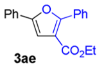
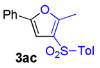
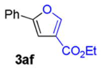
entry	diazo	temp (°C)	**3**: yield (%)[b]	**4**: yield (%)[b]
1	 **2a**	25	**3aa**: 31%	**4aa**: 69%
2		80	**3aa**: 68%	**4aa**: 30%
3	 **2b**	25	**3ab**: 13%	**4ab**: trace
4		80	**3ab**: 91%	**4ab**: trace

[a] Reactions were carried out under N_2 with 1.0 equiv of diazo reagent and 2.0 equiv of **1a** in one-time fashion without slow addition of the diazo reagent. [b] Isolated yields.

[Co(**P1**)] was shown to be effective in catalyzing the cyclization of **1a** with various A/A-substituted diazo reagents at 80 °C, producing 2,3,5-trisubstituted furans with complete regioselectivity (Table 2). In addition to diazoacetates **2a** and **2b**, which formed the corresponding furans through cyclization with the ester groups (entries 1 and 2), ketones could also effectively participate in the catalytic furan formation process, as demonstrated by diazoketone **2c**, which produced tosyl-substitued furan **3ac** in 87% yield (entry 3). More interestingly, α-ketodiazoacetates **2d** and **2e** selectively cyclized with **1a** to form furyl esters **3ad**[15c] and **3ae**, respectively (entries 4 and 5), indicating preferential involvement of the ketone carbonyl over the ester carbonyl. A similar preference for aldehyde carbonyls over ester carbonyls was also observed. For example, when formyldiazoacetate **2f** was employed, 2,4-disubstituted furan **3af** was isolated as the sole furan product in 80% yield through regioselective cyclization involving the aldehyde group (entry 6).

Table 2. [Co(P1)]-Catalyzed Formation of Multisubstituted Furans from Cyclization of Phenylacetylene with Various Acceptor/Acceptor-Substituted Diazo Reagents[a]



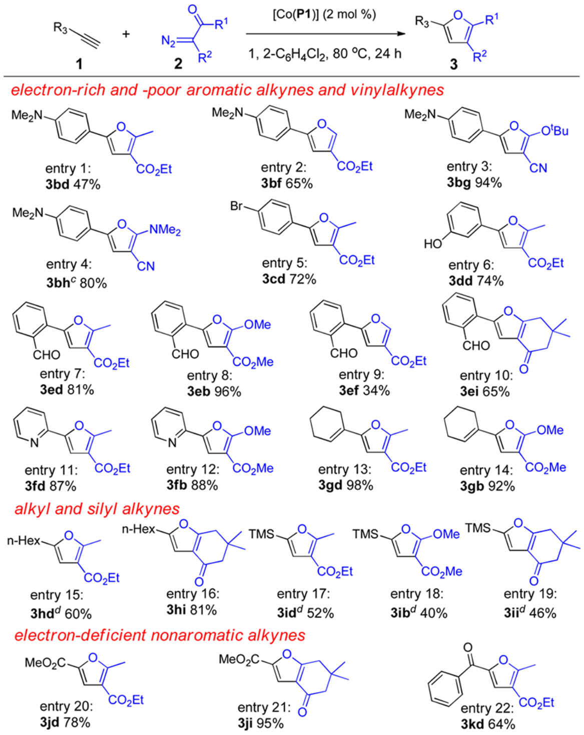
entry	diazo	furan	yield (%)[b]	entry	diazo	furan	yield (%)[b]
1	 **2a**	 **3aa**	68	4	 **2d**	 **3ad**	73
2	 **2b**	 **3ab**	91	5	 **2e**	 **3ae**	68
3	 **2c**	 **3ac**	87	6	 **2f**	 **3af**	80

[a] Reactions were carried out under N_2 with 1.0 equiv of diazo reagent and 2.0 equiv of **1a** in one-time fashion without slow addition of the diazo reagent. [b] Isolated yields.

After the successful cyclization of **1a** with diazo reagents to give furans, we investigated the alkyne scope of the [Co(**P1**)]-catalyzed radical cyclization in combination with different A/A-substituted diazo reagents.[16] The Co(II)-based metalloradical system was not only effective with acetylenes having different electronic properties but also tolerated many functional groups that would lead to side reactions in ionic processes (Table 3). For example, 4-(N,N-dimethylamino)phenylacetylene was fruitfully converted to 2,3,5-trisubstituted and 2,4-disubstituted furans through cyclization with different diazocarbonyls [entries 1−4; for the single-crystal structure of **3bh**, see the Supporting Information (SI)] without affecting the basic, electron-rich NMe_2 group. Arylacetylenes containing halogen and unprotected hydroxyl groups were also regioselectively cyclized by [Co(**P1**)] to form furans in good yields (entries 5 and 6). The functional group tolerance of the Co(II)-based radical process was further demonstrated by reactions of substrates containing unprotected aldehyde groups. For example, cyclizations of 2-formylphenylacetylene with various diazo reagents, including **2f**, resulted in the formation of aldehyde-containing furans in up to 96% yield (entries 7−10). Moreover, the Co(II)-catalyzed system could be extended to heteroaromatic and vinyl acetylenes, which formed the corresponding 2,3,5-trisubstituted furans in high yields (entries 11−14).

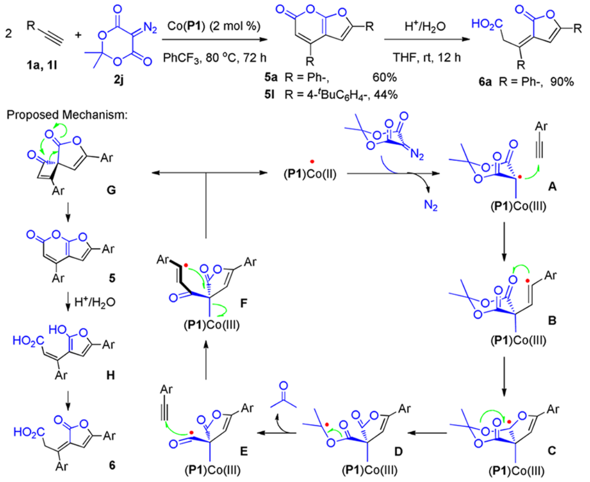
In addition to conjugated acetylenes, the Co(II)-based metalloradical cyclization is applicable to alkyl- and silylacetylenes (Table 3). For example, 1-octyne was effectively cyclized with different A/A-substituted diazo reagents to form the corresponding furans in good yields (entries 15 and 16). Under similar conditions, trimethylsilylacetylene was successfully cyclized to produce furans bearing a −TMS group (entries

Table 3. Synthesis of Multisubstituted Furans by [Co(P1)]-Catalyzed Metalloradical Cyclizations of Different Combinations of Alkynes and Diazo Reagents[a,b]



[a] Reactions were carried out under N_2 with 1.0 equiv of diazo reagent and 2.0 equiv of acetylene in one-time fashion without slow addition of the diazo reagent. [b] Isolated yields are shown. [c] The structure was determined by anomalous-dispersion effects in X-ray diffraction measurements on the crystal. [d] At 100 °C for 24 h.

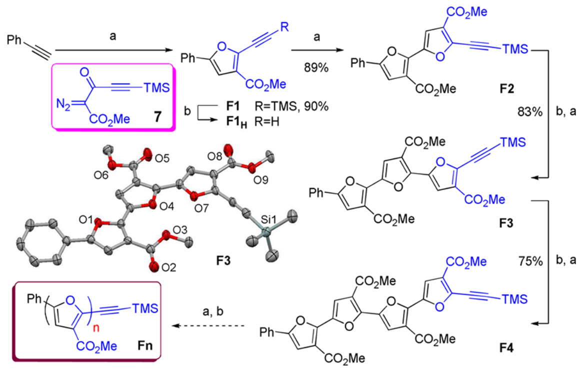
Scheme 2. Direct Construction of 6*H*-Furo[2,3-*b*]pyran-6-one Structures from Metalloradical Bicyclization of Alkynes with 5-Diazo-Meldrum's Acid Catalyzed by [Co(P1)]



17−19), which could potentially be deprotected to generate 2,3-substituted furans or replaced with other groups to form new furan derivatives. More significantly, ethynyl ester and ketone derivatives underwent the Co(II)-catalyzed furan cyclization in good to excellent yields (entries 20−22). This represents the first catalytic system that cyclizes electron-deficient alkynes with both cyclic and acyclic diazo reagents to form furan derivatives.

With appropriate diazo reagents, the Co(II)-based metalloradical cyclization can be carried out in tandem with 2 equiv of alkyne, leading to the construction of O-biheterocycles with interesting structures. For example, with 5-diazo-Meldrum's acid **2j**, a cyclic *α*-diazoacetate that has not been previously shown to cyclize with acetylenes to form heterocycles, 2 equiv of arylacetylenes **1a** and **1l** were successfully cyclized by [Co(**P1**)] to form bicyclic 6*H*-furo[2,3-*b*]pyran-6-ones **5a** and **5l**, respectively (Scheme 2). The formation of O-biheterocycles **5** can be properly rationalized on the basis of the proposed metalloradical cyclization mechanism (Scheme 1, cycle II). As detailed in Scheme 2, the tertiary radical intermediate **C** generated from the initial sequence of consecutive radical additions (**A** → **B** → **C**) undergoes radical fragmentation via consecutive radical scission of two *β*-C−O bonds (**C** → **D** → **E**) to give the key acyl radical intermediate **E**.[17] The release of acetone, which was confirmed experimentally (see the SI), presumably drives the radical *β*-scission of the two C−O bonds rather than the Co−C bond in **C**. Further radical addition−substitution of **E** with another alkyne molecule affords spiro compound **G**, which rearranges to the thermally more stable product **5**.[18] The nature of **5a** was further established by X-ray structure analysis of its derivative **6a** (see the SI), which was readily obtained from **5a** via hydrolysis and isomerization (Scheme 2).

Scheme 3. Construction of Functionalized *α*-Oligofurans via Iterative Metalloradical Cyclization of 7[a]



[a] Conditions: (a) 7, [Co(**P1**)] (5 mol %), 1,2-$C_6H_4Cl_2$, 80 °C, 48 h; (b) K_2CO_3, MeOH, 15 min.

Because of their great potential as organic electronic materials, oligofurans have attracted increasing interest.[2] While *α*-oligofurans have recently been prepared from presynthesized furan monomers through coupling reactions,[2d] their direct synthesis from acyclic precursors, an approach that would be highly attractive, has remained largely underdeveloped. As an application of the Co(II)-based metalloradical cyclization, we developed an iterative radical cyclization process to construct functionalized *α*-oligofurans with different numbers of furan units (Scheme 3). The key to its success is the design and synthesis of bifunctional ketodiazoacetate **7** bearing a TMS-protected internal alkyne unit, which was effectively cyclized with **1a** by [Co(**P1**)] to afford furan monomer **F1** without affecting the internal triple bond. Monomer **F1** was readily desilylated with K_2CO_3 to provide $\mathbf{F1_H}$, whose terminal alkyne could be cyclized again with **7** to afford *α*-furan dimer **F2**. Iteration of the desilylation and cyclization steps should afford functionalized *α*-oligofurans with specific numbers of repeating units and well-defined structures, as successfully demonstrated by the synthesis of α-furan trimer **F3** and tetramer **F4** (Scheme 3). The single-crystal structure of **F3** clearly revealed a highly planar conformation in spite of the presence of the ester functionalities (Scheme 3; see the SI). Initial studies showed that solutions of **F2−4** in THF, which were highly fluorescent, gave optical spectra with structured absorption bands having longer wavelengths than **F1**. More interestingly, the absorption was further red-shifted as the number of furan units increased, indicating increasing conjugation in **F2−4** (Figure 1).

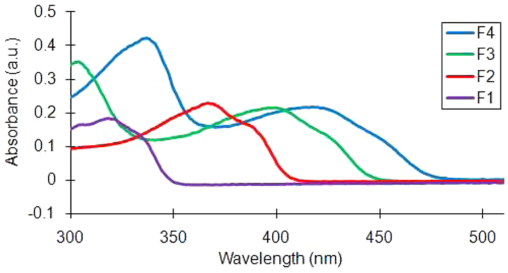


Figure 1. Optical spectra of α-oligofurans **F1−4** in THF.

In summary, we have developed a new Co(II) metalloradical-catalyzed system for the regioselective synthesis of furans by cyclization of alkynes with diazocarbonyls. This metalloradical cyclization has a wide substrate scope and an exceptionally high degree of functional group tolerance, permitting effective access to multisubstituted furans with diverse functionalities, and it was successfully applied to the construction of O-biheterocycles and α-oligofurans through double and iterative radical cyclization processes, respectively. This first demonstration of Co(II)-based metalloradical catalysis for five-membered heterocyclization involving tandem radical addition to $C\equiv C$ and $C=O$ bonds may stimulate the development of new catalytic radical cyclization processes for selective syntheses of more diverse carbo- and heterocycles.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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