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Enantioselective Cyclopropenation of Alkynes with Acceptor/Acceptor-Substituted Diazo Reagents via Co(II)-Based Metalloradical Catalysis

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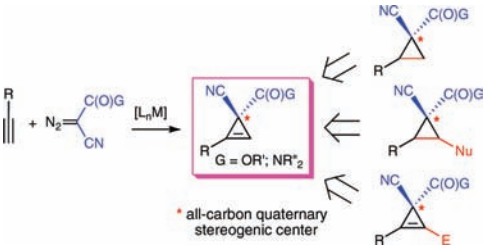
Supporting Information

ABSTRACT: The cobalt(II) complex of a new D_2-symmetric chiral porphyrin 3,5-diMes-ChenPhyrin, [Co(**P2**)], has been shown to be a highly effective chiral metalloradical catalyst for enantioselective cyclopropenation of alkynes with acceptor/acceptor-substituted diazo reagents, such as α-cyanodiazoacetamides and α-cyanodiazoacetates. The [Co(**P2**)]-mediated metalloradical cyclopropenation is suitable to a wide range of terminal aromatic and related conjugated alkynes with varied steric and electronic properties, providing the corresponding trisubstituted cyclopropenes in high yields with excellent enantiocontrol of the all-carbon quaternary stereogenic centers. In addition to mild reaction conditions, the Co(II)-based metalloradical catalysis for cyclopropenation features a high degree of functional group tolerance.

Cyclopropenes are a unique class of carbocyclic compounds with unsaturated, highly strained three-membered ring structures. The combination of high strain and unsaturation renders cyclopropenes as versatile synthons for a wide variety of synthetic organic transformations.[1] Consequently, significant efforts have been devoted toward the synthesis of this class of molecules, especially optically active chiral cyclopropenes.[1,2] Of different methods, catalytic asymmetric cyclopropenation of alkynes with diazo reagents constitutes one of the most direct and general methods for stereoselective construction of this type of strained ring structure.[1,2] A number of catalytic systems based on dirhodium(II) complexes of chiral carboxamidate and carboxylate ligands have been successfully developed to catalyze enantioselective cyclopropenation using several different types of diazo reagents as carbene sources, including diazoacetates,[3,4] diazosulfones,[5] aryldiazoacetates,[6] and styryldiazoacetates.[7−9] While the existing chiral Rh_2 catalysts were shown to be highly effective with both acceptor- and donor/acceptor-substituted diazo regents, asymmetric cyclopropenation with acceptor/acceptor-substituted diazo reagents remains to be developed.[10] Owing to the presence of two electron-withdrawing groups at the α-carbon, this class of diazo reagents has inherent low reactivity with Lewis acidic metal catalysts toward formation of the corresponding metallocarbene intermediates. Even when they can be formed under forcing conditions, their subsequent reactions with substrates are often difficult in terms of controlling enantioselectivity due to the high electrophilicity of the acceptor/acceptor-substituted metallocarbenes.

Scheme 1. Synthesis of Cyclopropenes Bearing Geminal Nitrile and Carbonyl Functionalities and Their Further Potential Transformations



As stable metalloradicals with well-defined open-shell doublet d^7 electronic structure, cobalt(II) complexes of porphyrins, [Co(Por)], have emerged as a new class of carbene transfer catalysts for olefin cyclopropanation.[11] With the introduction of D_2-symmetric chiral porphyrins as supporting ligands,[11a,12] the Co(II)-based metalloradical catalysts [Co(D_2-Por*)] have been demonstrated to be highly effective for asymmetric cyclopropanation of a broad combination of olefin substrates and diazo reagents with excellent diastereo- and enantioselectivity,[13] including electron-deficient olefins[13b] and acceptor/acceptor-substituted diazo reagent.[13d,13g] It is evident that Co(II)-based metalloradical cyclopropanation possesses a distinct reactivity profile from the widely studied Rh_2- and Cu-based closed-shell systems. Recent detailed mechanistic study confirmed the involvement of an unusual Co(III)-carbene radical as the key intermediate and elucidated an unprecedented stepwise radical addition−substitution pathway for the Co(II)-catalyzed olefin cyclopropanation.[14] To further validate the concept of metalloradical catalysis (MRC), we envisioned the possibility of Co(II)-based catalytic process for alkyne cyclopropenation if the radical addition−substitution pathway of the Co(III)-carbene radical intermediate could be also operative for alkynes in a similar way to alkenes. To address the aforesaid challenges in the area, we decided to target α-cyanodiazoacetates and α-cyanodiazoacetamides, two types of common acceptor/acceptor-substituted diazo reagents that have not been previously applied for asymmetric cyclopropenation (Scheme 1).[10] These catalytic processes would be synthetically attractive as the resultant multifunctionalized cyclopropenes bearing an all-carbon quaternary

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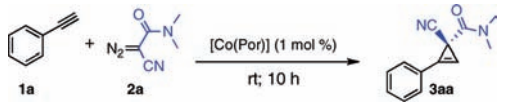
Table 1. Reaction Conditions for Cyclopropenation of Phenylacetylene with α-Cyano(*N*,*N*-dimethyl)diazoacetamide by Cobalt(II) Porphyrins[a]



entry	[Co(Por)][b]	solvent	yield (%)[c]	ee (%)[d]
1	[Co(TPP)]	$PhCF_3$	<5	–
2	[Co(**P1**)]	$PhCF_3$	10	71
3	[Co(**P2**)]	$PhCF_3$	95	82
4	[Co(**P2**)]	PhC1	40	nd[e]
5	[Co(**P2**)]	PhF	38	nd[e]
6	[Co(**P2**)]	PhMe	26	nd[e]
7	[Co(**P2**)]	PhH	45	nd[e]
8	[Co(**P2**)]	CH_2C1_2	<5	nd[e]
9	[Co(**P2**)]	$CC1_4$	70	77

[a] Reactions were carried out at room temperature for 10 h in one-time fashion without slow addition of the diazo reagent using 1 mol % [Co(Por)] under N_2 with 1.0 equiv of α-cyanodiazo(*N*,*N*-dimethyl) acetamide and 1.5 equiv of phenylacetylene. Concentration: 0.10 mmol diazo/mL. [b] See Figure 1 for structure. [c] Isolated yields. [d] Enantiomeric excess determined by chiral HPLC. [e] Not determined.

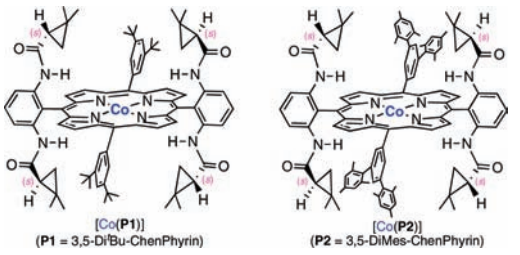


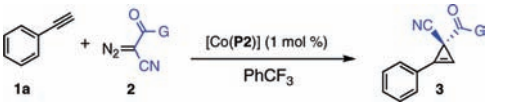
Figure 1. Structures of D_2-symmetric chiral cobalt(II) porphyrins.

stereogenic center can serve as invaluable chiral synthons for a range of stereoselective synthetic applications (Scheme 1).[1,2]

As the outcome of the effort, we report herein a highly efficient catalytic system based on a new chiral Co(II) metalloradical catalyst for enantioselective cyclopropenation of alkynes with both α-cyanodiazoacetates and α-cyanodiazoacetamides. In addition to high enantioselectivity, the Co(II)-catalyzed cyclopropenation can operate at room temperature using a stoichiometric ratio of reactants without the need of slow addition of the diazo reagents. Furthermore, the metalloradical catalytic process features a remarkable degree of tolerance toward various functionalities, including CHO, OH, and NH_2 groups.

Initial experiments were focused on the evaluation of ligand and solvent effects on cyclopropenation of phenylacetylene (**1a**) with α-cyano(*N*,*N*-dimethyl)diazoacetamide (**2a**) by [Co(Por)] under conditions that were deemed most practical: 1 mol % catalyst loading; room temperature; stoichiometric ratio of reactants; and one-time protocol without slow addition (Table 1). While the ineffectiveness of [Co(TPP)] for the reaction might be expected due to the absence of the H-bonding donor amide units (entry 1), we were somewhat surprised by the inferior performance of [Co(**P1**)] (Figure 1; entry 2), which has been previously shown to be highly effective for various cyclopropanation reactions.[12,13] This result indicated different requirements of catalyst

Table 2. [Co(P2)]-Catalyzed Enantioselective Cyclopropenation of Phenylacetylene with Acceptor/Acceptor-Substituted Diazo Reagents[a]



entry	diazo	cyclopropene	yield (%)[b]	ee (%)[c]
1[d]	2a	3aa	95	82
2[e]	2b	3ab	92	80
3[d]	2c	3ac	89	83
4[d]	2d	3ad	96	96
5[d]	2e	3ae	77	93
6[d]	2f	3af	76	98[f]

[a] Reactions were carried out in one-time fashion without slow addition of the diazo reagent using 1 mol % [Co(**P2**)] under N_2 with 1.0 equiv of diazo reagent and 1.5 equiv of phenylacetylene. Concentration: 0.10 mmol diazo/mL $PhCF_3$. [b] Isolated yields. [c] Enantiomeric excess determined by chiral HPLC. [d] At room temperature for 12 h. [e] At 40 °C for 24 h. [f] [*R*] absolute configuration determined by anomalous-dispersion effects in X-ray diffraction measurements on the crystal.

environment for the two carbene transfer processes and prompted us to develop new catalysts by taking advantage of the modular design and tunability of the D_2-symmetric chiral porphyrin system.[11a,12] To this end, replacement of the aliphatic *t*-butyl substituent in **P1** with aromatic mesityl group led to the design and synthesis of new D_2-symmetric chiral porphyrin 3,5-diMes-ChenPhyrin (**P2**; Figure 1). Gratifyingly, [Co(**P2**)] was found to be a highly effective catalyst for the reaction, leading to the formation of the desired 1,1-cyclopropeneamidonitrile **3aa** in 95% yield and 82% ee (entry 3). During the process of optimizing the reaction conditions, trifluorotoluene was shown to be the solvent of choice and performed significantly better than other solvents screened (entries 4–9).

The [Co(**P2**)]-based metalloradical cyclopropenation system was found to be applicable for different acceptor/acceptor-substituted diazo reagents under the similar practical conditions (Table 2). Like the *N*,*N*-dimethyl diazo **2a** (entry 1), *N*,*N*-diethyl analog **2b** could also function as effective carbene source for Co(II)-catalyzed enantioselective cyclopropenation of **1a** (entry 2). Notably, the catalytic system went equally well with *N*-methoxy-*N*-methyl α-cyanodiazoacetamide **2c**, providing the corresponding chiral cyclopropenyl Weinreb amide **3ac** (entry 3), which can serve as a potential synthon for preparation of chiral cyclopropenyl

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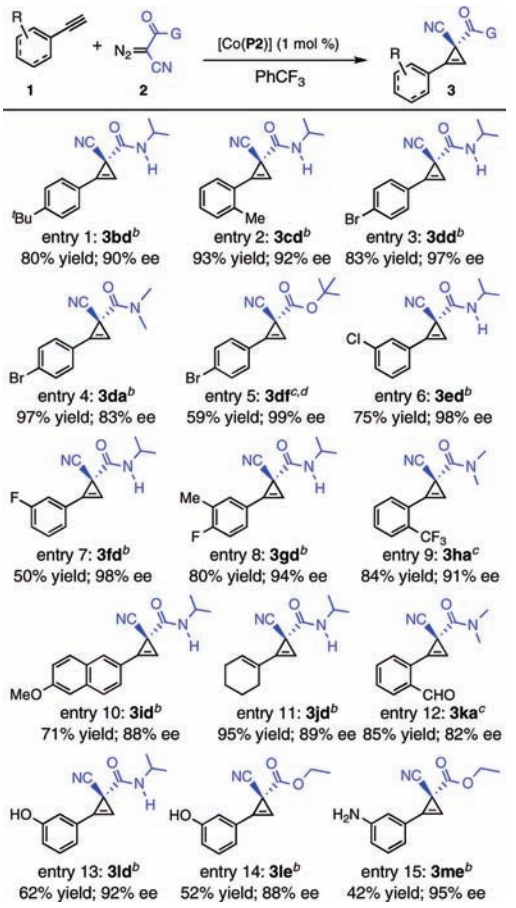
Table 3. [Co(P2)]-Catalyzed Asymmetric Cyclopropenation of Different Combinations of Aryl/Vinyl Alkynes and A/A-Type Diazo Reagents[a]

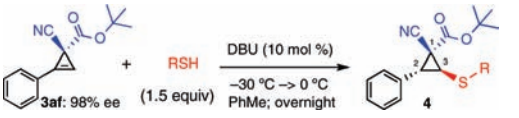


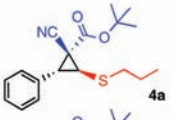
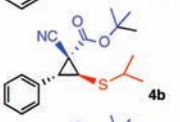
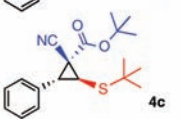
[a] Reactions were carried out in one-time fashion without slow addition of the diazo reagent using 1 mol % [Co(**P2**)] under N_2 with 1.0 equiv of diazo reagent and 1.5 equiv of phenylacetylene. Concentration: 0.10 mmol diazo/mL $PhCF_3$; Isolated yields; Enantiomeric excess determined by chiral HPLC. [b] At room temperature for 12 h. [c] At 40 °C for 24 h. [d] [*R*] absolute configuration; see footnote f of Table 2.

cyanoaldehyde and cyanoketone derivatives.[15] In addition to the tertiary analogs, secondary α-cyanodiazoacetamides could also be productively used as exemplified with *N*-isopropyl α-cyanodiazoacetamide **2d**, forming the desired cyclopropene **3ad** in 96% yield and 96% ee (entry 4). Besides α-cyanodiazoacetamides, [Co(**P2**)] was shown to enable cyclopropenation with α-cyanodiazoacetates as well. For example, both ethyl and *t*-butyl α-cyanodiazoacetates (**2e** and **2f**) could be effectively utilized to cylopropenate **1a** to form 1,1-cyclopropeneesternitrile **3ae** and **3af**, respectively, in good yields and excellent enantioselectivities (entries 5 and 6). The absolute configuration of the all-carbon quaternary stereogenic center in **3af** was established as [*R*] by X-ray crystal structural analysis (see Supporting Information).

The [Co(**P2**)]-catalyzed asymmetric cyclopropenation could be successfully expanded for a wide range of terminal aromatic and related conjugated alkynes in combination with various acceptor/acceptor-substituted diazo reagents (Table 3). For example, using *N*-isopropyl diazo **2d** as the carbene source, enantioselective cyclopropenation reactions

Table 4. Diastereoselective Thiol Addition to Cyclopropenes[a]



entry	thiol	product	yield (%)[b]	ee (%)[c]
1		 4a	98	98[d]
2		 4b	88	98
3[e]		 4c	54	98

[a] Reactions were carried out overnight in toluene using 10 mol % DBU with 1.0 equiv of cyclopropene **3af** (98% ee) and 1.5 equiv of thiol. The reaction temperature was initially at −30 °C and gradually warmed to room temperature. [b] Isolated yields of single diastereomers. [c] Enantiomeric excess determined by chiral HPLC. [d] [1*S*,2*R*,3*S*] absolute configuration determined by anomalous-dispersion effects in X-ray diffraction measurements on crystal. [e] 100 mol % DBU; room temperature; 48 h .

of phenylacetylenes substituted with alkyl groups at different positions proceeded equally well as phenylacetylene (entries 1 and 2). In addition, various halogenated phenylacetylenes could be enantioselectively cyclopropenated with both α-cyanodiazoacetamides and -acetates (entries 3−8). Among the chiral cyclopropene products, the absolute configuration of the all-carbon quaternary stereogenic center in **3df** (entry 5) was established to be [*R*] by X-ray crystal structural analysis (see Supporting Information). Chiral cyclopropene derivatives from reactions of aromatic alkynes containing both electron-withdrawing and -donating groups could also be obtained in good yields and high enantioselectivities (entries 9 and 10). The Co(II)-catalyzed reaction could be extended for nonaromatic conjugated alkynes as demonstrated with cyclopropenation reaction of cyclohexenylethyne with diazo **2d** for the high-yielding formation of enantioenriched 1,1-cyclopropeneamidonitrile **3jd** (entry 11).

Consistent with the proposed radical mechanism of nonelectrophilic carbene radical intermediate,[14] the Co(II)-catalyzed carbene transfer process was found to tolerate functional groups that would otherwise undergo ylide-type chemistry associated with electrophilic metallocarbenes. For example, the aldehyde functionality could be tolerated without complication from potential ylide-mediated epoxidation (entry 12). The functional group tolerability of [Co(**P2**)]-catalyzed asymmetric cyclopropenation was further highlighted by the reactions of phenylacetylene derivatives containing hydroxyl and amino substituents (entries 13−15). In all the cases, no O−H or N−H insertion products were observed.

The above demonstrated cyclopropenation process via [Co(**P2**)]-based metalloradical catalysis presents a viable route to access densely functionalized cyclopropenes containing enantioenriched all-carbon quaternary stereogenic centers, which should find a range of applications as chiral building blocks for stereoselective organic syntheses through further functional group transformations. For instance, they can be transformed to highly functionalized

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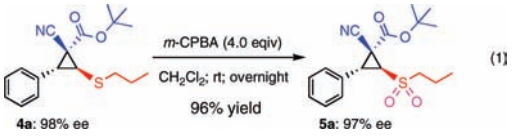
cyclopropane derivatives by nucleophilic or electrophilic addition to the activated π-bonds as a result of the high ring strain.[1,2] In particular, nucleophilic addition with soft nucleophiles would provide an entry to chiral heterosubstituted cyclopropanes, which would be difficult or impossible to access via direct asymmetric cyclopropanation of alkenes. As an initial effort toward this type of applications, we demonstrated that cyclopropene **3af** could undergo highly diastereoselective addition reactions with thiol nucleophiles to furnish heterosubstituted cyclopropane derivatives (Table 4).[16] For example, when **3af** in 98% ee was treated with 1.5 equiv of *n*-propanethiol, the corresponding 1,1,2,3-tetra-substituted cyclopropane **4a** could be isolated in 98% yield as a sole diastereomer in the same high optical purity (entry 1). The absolute configuration of the three continuous stereogenic centers in **4a** was established to be [1*S*,2*R*,3*S*] by X-ray crystal structural analysis (see Supporting Information). Highly diastereoselective addition reactions of **3af** could be similarly accomplished with isopropanethiol and *tert*-butylthiol, affording enantiopure thiolated cyclopropanes **4b** and **4c**, respectively, albeit in relatively lower yields due to the higher steric hindrance (entries 2 and 3).

Furthermore, we showed that the thiolated cyclopropane **4a** could be oxidatively converted to cyclopropyl sulfone **5a** in a high yield without loss of its optical purity upon simple treatment with *m*-chloroperbenzoic acid (CPBA) at room temperature (eq 1).



(1)

In summary, we have developed a highly enantioselective process based on the new metalloradical catalyst [Co(**P2**)] for cyclopropenation of aryl/vinyl alkynes with both α-cyanodiazoacetamides and α-cyanodiazoacetates. It represents the first successful applications of these two types of acceptor/acceptor-substituted diazo reagents for asymmetric cyclopropenation,[10] providing a practical method for the preparation of multifunctionalized cyclopropenes bearing enantioenriched all-carbon quaternary stereogenic centers that may serve as useful chiral synthons for stereoselective synthesis (Scheme 1). Among several salient features, the Co(II)-based system enjoys an unusual degree of functional group tolerance, which is believed to have close relevance to the radical pathway of Co(II)-based metalloradical catalysis.[14]

■ ASSOCIATED CONTENT

Supporting Information. Experimental details and analytical data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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