Asymmetric Radical Cyclopropanation of Alkenes with In Situ-Generated Donor-Substituted Diazo Reagents via Co(II)-Based Metalloradical Catalysis

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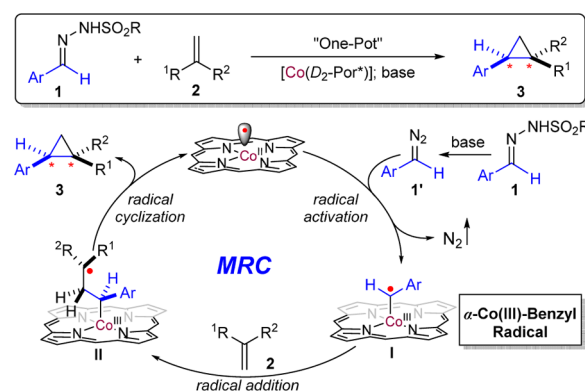[‡]Department of Chemistry, University of South Florida, Tampa, Florida 33620, United States

S Supporting Information

ABSTRACT: Donor-substituted diazo reagents, generated in situ from sulfonyl hydrazones in the presence of base, can serve as suitable radical precursors for Co(II)-based metalloradical catalysis (MRC). The cobalt(II) complex of D_2-symmetric chiral porphyrin [Co(3,5-Di^{t}Bu-Xu(2′-Naph)Phyrin)] is an efficient metalloradical catalyst that is capable of activating different N-arylsulfonyl hydrazones for asymmetric radical cyclopropanation of a broad range of alkenes, affording the corresponding cyclopropanes in high yields with effective control of both diastereo- and enantioselectivity. This Co(II)-based metalloradical system represents the first catalytic protocol that can effectively utilize donor-type diazo reagents for asymmetric olefin cyclopropanation.

Scheme 1. Proposed Pathway for Asymmetric Radical Cyclopropanation with Donor-Substituted Diazo Reagents

There has been lasting interest in devising strategies to control stereoselectivity, especially enantioselectivity, of radical reactions for applications in organic synthesis.[1] Among recent advances,[1,2] metalloradical catalysis (MRC), which aims at the development of metalloradical-based systems for both catalytic initiation and selective control of radical processes, has led to the discovery of new catalytic pathways for stereoselective radical reactions.[3,4] As stable metalloradicals, cobalt(II) complexes of D_2-symmetric chiral amidoporphyrins [Co(D_2-Por*)] have emerged as effective catalysts for asymmetric radical transformations through catalytic generation of metal-stabilized organic radicals, such as the fundamentally new α-metalloalkyl radicals and α-metalloaminyl radicals, as the key intermediates.[5] To date, Co(II)-based metalloradical catalysis (Co(II)-MRC) has exhibited capability of activating both acceptor- and acceptor/acceptor-substituted diazo reagents to generate corresponding α-Co(III)-alkyl radicals (also known as Co-(III)-carbene radicals) as key intermediates for various C-centered radical processes, including radical cyclopropanation of alkenes.[6,7] Studies suggest that potential H-bonding interactions between carbonyl groups of these types of diazo reagents and the amide units of the porphyrin ligands in the resulting α-Co(III)-alkyl radicals play an important role in enhancing reactivity and controlling stereoselectivity. It was unclear if Co(II)-MRC could also be applicable to other types of diazo reagents that lack a carbonyl group, such as donor-substituted diazo reagents. Specifically, we wondered whether [Co(D_2-Por*)] metalloradical catalysts were able to activate aryldiazo-

methanes to generate the corresponding α-Co(III)-benzyl radical intermediate **I** (Scheme 1). In the absence of carbonyl functionalities, what element of interaction could be explored for the effective control of enantioselectivity in the subsequent radical addition of the α-Co(III)-benzyl radical **I** to the olefin substrate? Furthermore, would the final step, 3-*exo-tet* radical cyclization of the resulting γ-Co(III)-alkyl radicals **II**, be diastereoselective? Additional questions arose from the intrinsic instability of donor-substituted diazomethanes, which are typically generated in situ from stable sulfonyl hydrazone precursors.[8] Would the Co(II)-MRC system be compatible with the basic conditions required for the in situ generation protocol? If these questions could be answered positively, it would further expand the application of Co(II)-based radical cyclopropanation for the catalytic synthesis of enantioenriched 1,2-bisaryl and related cyclopropane compound **3**.

Asymmetric olefin cyclopropanation with diazo reagents represents one of the most general methods for the construction of optically active three-membered carbocycles.[9] While tremendous progress has been made with the use of several types of diazo reagents, asymmetric cyclopropanation with donor-substituted diazo reagents has been much less developed.[10] As a novel alternative involving the further transfer of the initially formed electrophilic Rh$_2$-carbenes into nucleophilic chiral sulfur ylides, Aggarwal and co-workers
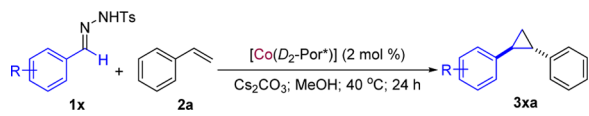
developed an indirect approach for asymmetric cyclopropanation with sulfonyl hydrazones as diazo precursors using the combination of dirhodium carboxylates and chiral sulfides as the catalyst that works specifically for electron-deficient olefins.[8c,10b] Nevertheless, it would be desirable to develop new catalytic systems that are capable of direct asymmetric cyclopropanation of diverse alkenes with donor-substituted diazo reagents.[11] In view of the radical pathway of MRC (Scheme 1), we hypothesized that the radical cyclopropanation approach could potentially address the aforementioned issues with donor-substituted diazo reagents because a neutral radical process is generally less sensitive to electronic effects. Herein, we wish to report the development of the first asymmetric catalytic system that is highly effective for direct cyclopropanation of alkenes with α-aryl diazomethanes.

Our study began with cyclopropanation of styrene (2a) with benzaldehyde tosylhydrazone (1a), which is known to generate α-phenyldiazomethane under basic conditions (Table 1). Even

Table 1. Asymmetric Cyclopropanation of Styrene with Tosylhydrazones by Metalloradical Catalysts [Co(D₂-Por*)] ^{a}

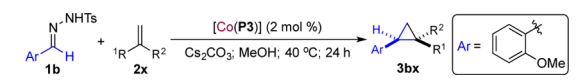| entry	R	catalyst	product	yield (%)^b	dr^c	ee (%)^d
1	H (1a)	[Co(TPP)]	3aa	46	88:12	-
2	H (1a)	[Co(P1)]	3aa	64	89:11	-42
3	H (1a)	[Co(P2)]	3aa	65	78:22	<5
4	H (1a)	[Co(P3)]	3aa	67	95:5	26
5	2-MeO (1b)	[Co(P3)]	3ba	78	95:5	99
6	2-Et (1c)	[Co(P3)]	3ca	87	85:15	33
7	4-MeO (1d)	[Co(P3)]	3da	23	93:7	23
8	3-MeO (1e)	[Co(P3)]	3ea	69	95:5	23
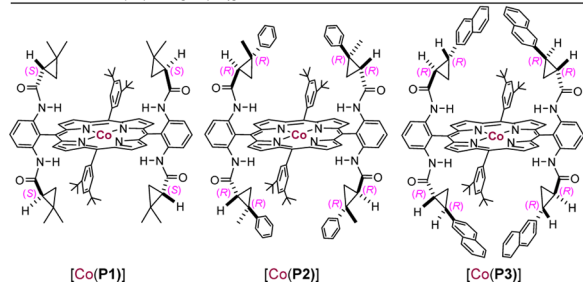
[Co(P1)]   [Co(P2)]   [Co(P3)]

^{a}Carried out with 1x (0.1 mmol) and 2a (1.5 equiv) in the presence of Cs₂CO₃ (2 equiv) in methanol (0.6 mL). ^{b}Isolated yields. ^{c}Determined by ^{1}H NMR. ^{d}Determined by chiral HPLC for the major *trans* diastereomer.
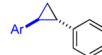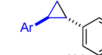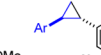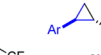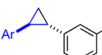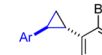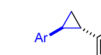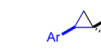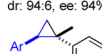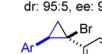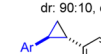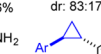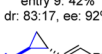
simple metalloradical catalyst [Co(TPP)] (TPP = 5,10,15,20-tetraphenylporphyrin) could catalyze the reaction in the presence of Cs₂CO₃ in methanol, forming the desired 1,2-diphenyl cyclopropane 3aa in 46% yield (entry 1). This result signifies the compatibility of the Co(II)-based metalloradical system with the use of both bases and polar solvents. The stereoselectivity of the reaction was then evaluated by using Co(II) complexes of D_2-symmetric chiral amidoporphyrins [Co(D₂-Por*)]. When the first-generation catalyst [Co(P1)] (P1 = 3,5-Di^{t}Bu-ChenPhyrin) was used,[6f] 3aa could form in higher yield with a significant level of both enantio- and diastereoselectivity (entry 2). To further improve the catalytic reaction, we then turned our attention to the second-generation Co(II)-based metalloradical catalysts.[6b] While the phenyl-

substituted [Co(P2)] (P2 = 3,5-Di^{t}Bu-QingPhyrin) was less selective, the naphthyl-substituted [Co(P3)] (P3 = 3,5-Di^{t}Bu-Xu(2′-Naph)Phyrin)) could effectively catalyze the formation of 3aa with excellent diastereoselectivity but lower enantioselectivity (entry 4). It should be noted that comparable reactivity was observed with the use of preformed α-phenyldiazomethane (see Table S1 in Supporting Information (SI)). The ineffective asymmetric indu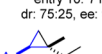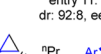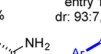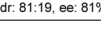ction is likely attributed to the low-barrier rotation of the α-benzyl radical unit around the Co(III)−C σ bond in intermediate I (Scheme 1) that diminishes its approaching preference to the prochiral styrene substrate between the *re* and *si* faces. To restrict the rotation, we decided to use the benzaldehyde tosylhydrazone derivative that contains an *ortho*-methoxy group (1b). Considering the MeO group is known as a good hydrogen bond acceptor,[12] we postulated that the potential formation of the N−H···O hydrogen bond between the amido group of the chiral ligand and the MeO group of tosylhydrazone 1b (Figure S1 in SI) might rigidify the resulting intermediate I, leading to improved stereoselectivity. Indeed, the corresponding cyclopropane 3ba was obtained in good yield (78%) with high diastereoselectivity (95:5 dr) and excellent enantioselectivity (99% ee) (entry 5; see Table S2 in SI for detailed solvent effect). Conversely, asymmetric induction of the cyclopropanation process was significantly reduced when the MeO group in 1b was replaced by a sterically comparable Et group despite the high reactivity (entry 6). Moreover, low enantioselectivity was observed when the MeO group in 1b was moved from the *ortho*- to either the *meta*- or *para*-position of the phenyl ring although with similarly high diastereoselectivity (entries 7 and 8). These results seem to support the hypothesized hydrogen-bonding interaction.

Under the optimized conditions, the scope of the [Co(P3)]/1b-based catalytic system was then evaluated by employing different alkenes (Table 2). Like styrene, its derivatives bearing substituents with different electronic properties, including electron-donating MeO and electron-withdrawing CF₃ groups,

Table 2. Asymmetric Cyclopropanation of Different Olefins with Tosylhydrazone 1b Catalyzed by [Co(P3)] ^{a}

3ba entry 1^b: 83% dr: 95:5, ee: 99%	**3bb** entry 2: 88% dr: 95:5, ee: 94%	**3bc** entry 3: 81% dr: 96:4, ee: 93%	**3bd** entry 4^c: 85% dr: 94:6, ee: 94%
3be entry 5: 85% dr: 94:6, ee: 94%	**3bf** entry 6: 89% dr: 95:5, ee: 96%	**3bg** entry 7^d: 61% dr: 90:10, ee: 96%	**3bh** entry 8: 90% dr: 83:17, ee: 93%
3bi entry 9: 42% dr: 83:17, ee: 92%	**3bj** entry 10: 71% dr: 75:25, ee: 95%	**3bk** entry 11: 69% dr: 92:8, ee: 97%	**3bl** entry 12: 68% dr: 93:7, ee: 99%
3bm entry 13: 77% dr: 81:19, ee: 81%	**3bn** entry 14: 50% dr: 78:22, ee: 89%	**3bo** entry 15: 49% dr: 83:17, ee: 91%	**3bp** entry 16: 41% dr: 71:29, ee: 77%	**3bq** entry 17^e: 42% dr: 75:25, ee: 82%

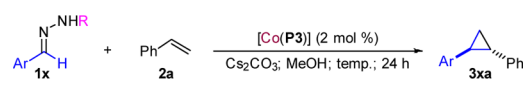^{a}Carried out with 1b (0.1 mmol) and 2x (1.5 equiv) in the presence of Cs₂CO₃ (2 equiv) in methanol (0.6 mL); isolated yields; dr was determined by ^{1}H NMR; ee of the major *trans* diastereomer was determined by chiral HPLC. ^{b}Performed on 1.0 mmol scale. ^{c}Absolute configuration was determined by X-ray as (1S, 2S). ^{d}5 mol % [Co(P3)]. ^{e}5.0 equiv of 2q.

could be cyclopropanated in high yields with excellent diastereo- and enantioselectivity (entries 1−3). Halogenated styrenes such as those with a Br atom at various positions were also shown to be suitable substrates for the catalytic process (entries 4−6). The relative and absolute configurations of cyclopropane **3bd** (entry 4) were established as *trans* and (1*S*,2*S*), respectively (see Figure S2 in SI). As demonstrated for 2-bromostyrene (**2f**) together with 2,4,6-trimethylstyrene (**2g**), sterically hindered styrene derivatives could also undergo productive cyclopropanation (entries 6 and 7). Furthermore, this system was also applicable for 1,1-disubstituted olefins as demonstrated with *α*-substituted styrene derivatives **2h**, **2i**, and **2j**, affording the desired cyclopropanes with enantioselective control of the newly formed quaternary stereogenic centers, albeit with moderate diastereoselectivity (entries 8−10). Distinctly, the Co(II)-based radical process could tolerate functional groups as exemplified by the highly enantioselective cyclopropanation of 3-aminostyrene (entry 11). In addition to the expanded aromatic olefins such as 2-vinylnaphthalene (entry 12), conjugated dienes, including both aromatic diene **2m** and aliphatic diene **2n**, could also be employed as substrates but with relatively lower stereoselectivities (entries 13 and 14). It was notable that both electron-rich and -deficient nonaromatic olefins, such as vinyl ether **2o**, acrylamide **2p**, and vinyl ketone **2q**, could be enantioselectively cyclopropanated as well (entries 15−17) with moderate control of stereoselectivities. The observed substrate scope and reactivity profile of [Co(**P3**)]-catalyzed cyclopropanation are in agreement with the underlying radical mechanism (Scheme 1). It was also noteworthy to mention that the one-pot protocol of the Co(II)-catalyzed cyclopropanation could be scaled up 10-fold as demonstrated with the high-yielding synthesis of cyclopropane **3ba** on 1.0 mmol scale without affecting the excellent stereoselectivity (entry 1).

Guided by the postulated hydrogen-bonding interaction in the key intermediates **I**, we then sought to identify other benzaldehyde sulfonylhydrazone derivatives as effective radical precursors for asymmetric cyclopropanation (Table 3). Like arylhydrazone **1b** (entry 1), 2,5-dimethoxybenzaldehyde-derived tosylhydrazone (**1f**) could be also effectively activated by [Co(**P3**)] for cyclopropanation of styrene, affording cyclopropane **3fa** in 91% yield with 90% de and 94% ee (entry 2). Remarkably, fluoroarene-based tosylhydrazones such as **1g**−**1j** were found to be even more active than **1b**, enabling the catalytic process even at rt (entries 3, 6, 8, and 10). The desired fluorine-containing bisaryl cyclopropanes **3ga**−**3ja** were obtained in up to 90% yield with 88−92% de and 68−88% ee. Attempts to further improve enantioselectivity, the low temperature asymmetric cyclopropanation was reexamined with the use of 2,6-difluorobenzaldehyde-derived (2,4,6-triisopropylphenyl)sulfonyl hydrazone **1g′**. Gratifyingly, the reaction could proceed effectively at 0 °C, affording **3ga** in 83% yield with considerably enhanced stereoselectivities (entry 5). Likewise, the reactions with related **1h′**−**1j′** could also be productively conducted at 0 °C, affording the cyclopropanes **3ha**−**3ja** with significantly improved diastereo- and enantioselectivity (entries 7, 9, and 11). Under the same conditions, while *o*-Cl-benzaldehyde-derived sulfonylhydrazone gave a similar result to **1h′**, *o*-Br- and *o*-I-benzaldehyde-derived sulfonyl hydrazones proved to be less effective radical precursors for the catalytic process (see Scheme S1 in SI).

To probe the underlying stepwise radical mechanism of the Co(II)-catalyzed cyclopropanation, both (*E*)- and (*Z*)-*β*-deuterostyrenes were employed as substrates (Scheme 2).
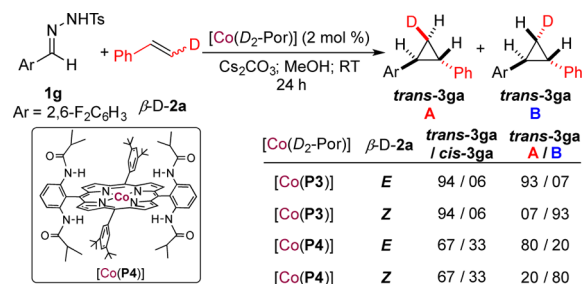
Table 3. Asymmetric Cyclopropanation of Styrene with Various Sulfonyl Hydrazones Catalyzed by [Co(P3)][a]

entry	Ar	R[b]	product	temp. (°C)	yield (%)[c]	dr[d]	ee (%)[e]
1	(2-OMe-phenyl)	Ts (**1b**)	**3ba**	40	78	95:5	99
2	(2,5-diOMe-phenyl)	Ts (**1f**)	**3fa**	40	91	95:5	94
3	(2,6-F₂-phenyl)	Ts (**1g**)	**3ga**	RT	90	94:6	86
4	(2,6-F₂-phenyl)	Ts (**1g**)	**3ga**	0	<10	-	-
5	(2,6-F₂-phenyl)	TPS (**1g′**)	**3g′a**	0	83	>99:1	93
6	(2-F-phenyl)	Ts (**1h**)	**3ha**	RT	58	96:4	71
7	(2-F-phenyl)	TPS (**1h′**)	**3h′a**	0	75	>99:1	76
8	(2,4,6-F₃-phenyl)	Ts (**1i**)	**3ia**	RT	85	96:4	88
9	(2,4,6-F₃-phenyl)	TPS (**1i′**)	**3i′a**	0	85	>99:1	93
10	(pentafluorophenyl)	Ts (**1j**)	**3ja**	RT	82	95:5	68
11	(pentafluorophenyl)	TPS (**1j′**)	**3j′a**	0	81	>99:1	89

[a]Carried out with **1x** (0.1 mmol) and **2a** (1.5 equiv) in the presence of Cs₂CO₃ (2 equiv) in methanol (0.6 mL). [b]Ts = 4-toluenesulfonyl; TPS = (2,4,6-triisopropyl)phenyl sulfonyl. [c]Isolated yields. [d]Determined by ¹H NMR. [e]Determined by chiral HPLC for the major *trans* diastereomer.

Scheme 2. Cyclopropanation of (E)- and (Z)-β-Deuterostyrenes To Probe Radical Reaction Mechanism

[Co(D₂-Por)]	β-D-**2a**	trans-**3ga** / cis-**3ga**	trans-**3ga** A / B
[Co(**P3**)]	*E*	94 / 06	93 / 07
[Co(**P3**)]	*Z*	94 / 06	07 / 93
[Co(**P4**)]	*E*	67 / 33	80 / 20
[Co(**P4**)]	*Z*	67 / 33	20 / 80

While a concerted mechanism is usually stereospecific, a stepwise radical mechanism (Scheme 1) would result in the formation of four possible diastereomers from either (*E*)- or (*Z*)-*β*-deuterostyrene: two *trans*-isotopomers **A** and **B** and two *cis*-isotopomers **C** and **D** due to the rotation of *β*-C−C bond in the *γ*-Co(III)-alkyl radical intermediate **II** before ring closure (Schemes S2 and S3 in SI). Using catalyst [Co(**P3**)], cyclopropanation of (*E*)-*β*-deuterostyrene with tosylhydrazone **1g** gave *trans*-**3ga** as the dominant product with a 93:7 ratio of isotopomers **A** and **B**. Under the same conditions, the reaction of (*Z*)-*β*-deuterostyrene resulted in the identical 93:7 ratio of isotopomeric distribution but in favoring **B** over **A**. The observation of *trans*-isotopomer **B** from (*E*)-*β*-deuterostyrene as well as *trans*-isotopomer **A** from (*Z*)-*β*-deuterostyrene is evidently a result of the rotation of the *β*-C−C bond in intermediate **II**. When sterically less hindered [Co(**P4**)] (**P4** = 3,5-Di*ᵗ*Bu-IbuPhyrin) was used as the catalyst,[13] a significantly different isotopomeric ratio of *trans*-isotopomers **A** and **B** (from 93:7 to 80:20) was observed, suggesting easier rotation of the *β*-C−C bond in a less-crowded ligand environment (Schemes S4 and S5 in SI). Together, these observations convincingly

support the proposed stepwise radical mechanism. Furthermore, experiments were performed for direct detection of the α-Co(III)-benzyl radical species **I** (Scheme 1) by high-resolution mass spectrometry (HRMS).[14] The exposure of $[\text{Co}(\textbf{P4})]$ to **1g** (10 equiv) with a base in methanol resulted in a mixture that was filtrated and analyzed by HRMS in the absence of any additives such as formic acids that commonly act as electron carriers for ESI ionization. As shown in Scheme S6 in SI, the obtained spectrum clearly revealed a signal corresponding to $[\text{Co}(\textbf{P4})\text{-}(2,6\text{-}F_2C_6H_3CH)]^+$ (m/z = 1361.6515), which resulted from the neutral α-Co(III)-benzyl radical **I** by the loss of one electron.

In summary, Co(II)-based metalloradical catalysis (MRC) has, for the first time, been successfully applied to donor-substituted diazo reagents, generated from *N*-arylsulfonyl hydrazones in the presence of a base, for olefin cyclopropanation. Chiral metalloradical complex $[\text{Co}(\textbf{P3})]$ has been shown to be an effective catalyst for asymmetric radical cyclopropanation with α-aryldiazomethane precursors. The Co(II)-based cyclopropanation is applicable to a broad combination of *N*-arylsulfonyl hydrazones and alkenes, affording the cyclopropane derivatives in high yields with excellent diastereo- and enantioselectivity.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b11336.

> Experimental details and analytical data for all new compounds (PDF)
> Crystallographic data (CIF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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