# Cu(I)-Catalyzed Diamination of Conjugated Dienes. Complementary Regioselectivity from Two Distinct Mechanistic Pathways Involving Cu(II) and Cu(III) Species

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Ⓢ *Supporting Information*

ABSTRACT: Conjugated dienes can be diaminated at the internal and/or terminal double bonds using Cu(I) as catalyst and *N,N*-di-*t*-butyldiaziridinone (**1**) as nitrogen source. The regioselectivity is highly dependent upon the choice of Cu(I) catalyst and the substituents on diene substrates. The diamination likely proceeds via two mechanistically distinct pathways. The N—N bond of *N,N*-di-*t*-butyldiaziridinone (**1**) is first homolytically cleaved by the Cu(I) catalyst to form four-membered Cu(III) species **A** and Cu(II) radical species **B**, which are in rapid equilibrium. The internal diamination likely proceeds in a concerted manner via Cu(III) species **A**, and the terminal diamination likely involves Cu(II) radical species **B**. Kinetic studies have shown that the diamination is first-order in *N,N*-di-*t*-butyldiaziridinone (**1**), zero-order in olefin, and first-order in total Cu(I) catalyst, and the cleavage of the N—N bond of **1** by the Cu(I) catalyst is the rate-determining step. The internal diamination is favored by use of CuBr without ligand and electron-rich dienes. The terminal diamination is favored when using CuCl—L and dienes with radical-stabilizing groups.
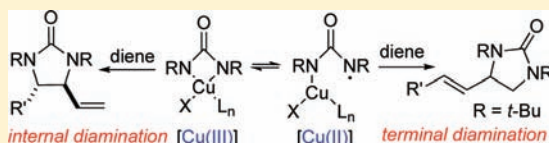
■ INTRODUCTION

Present in many biologically active compounds and chiral catalysts, 1,2-diamines are important functional moieties.[1] The synthesis of 1,2-diamines is of interest to organic chemists.[1] Diamination of olefins, allowing direct installation of two nitrogen atoms across C—C double bonds, provides a straightforward approach to prepare 1,2-diamines. Various metal-free,[1,2] metal-mediated,[1,3,4] and metal-catalyzed[4c,5−8] diaminations of olefins have been developed. In our own studies, we have developed Pd(0)-[9−11] and Cu(I)-catalyzed[12−15] diaminations of olefins using three-membered rings **1**−**3**[16−19] as nitrogen sources (Chart 1). When Pd(0) was used as catalyst, various dienes were efficiently diaminated at the internal double bonds with *N,N*-di-*t*-butyldiaziridinone (**1**) (Scheme 1).[9] Mechanistic studies suggest this diamination likely proceeds via a concerted reaction pathway.[9f] The Pd(0) catalyst inserts into the N—N bond of *N,N*-di-*t*-butyldiaziridinone (**1**) to form four-membered Pd(II) species **6**,[20] which reacts with diene **4** to give π-allyl Pd species **7**.[21,22] Species **7** then undergoes reductive elimination to give internal diamination product **5** and regenerate the Pd(0) catalyst.[23] However, when the CuCl—L complex was used as catalyst, the terminal diamination product **8** was predominantly formed for various conjugated dienes (Scheme 2).[12a] A radical mechanism has been proposed for this Cu(I)-catalyzed diamination.[12a] The Cu(I) first homolytically cleaves the N—N bond of *N,N*-di-*t*-butyldiaziridinone (**1**) to give nitrogen radical species **9**.[24−28] Radical species **9** adds to the terminal double bond of the diene to form allyl radical species **10**, which then undergoes rapid C—N bond formation to give terminal diamination product **8** and regenerate the Cu(I) catalyst. The CuCl—L catalyzed diamination

Chart 1
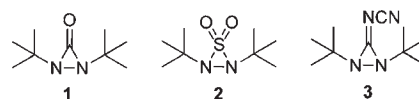
with *N,N*-di-*t*-butylthiadiaziridine 1,1-dioxide (**2**)[14] and *N,N*-di-*t*-butyl-3-(cyanimino)-diaziridine (**3**)[15] also appears to proceed via a stepwise radical mechanism based upon studies of deuterated olefin substrates.

Very recently, we have found that various conjugated dienes can be predominantly diaminated at internal double bonds when CuBr without a ligand is used as catalyst, giving internal diamination product **5** in good yield and high regioselectivity (Scheme 3).[29] The preliminary studies suggest that the Cu(I)-catalyzed diamination may proceed via two distinct pathways (Scheme 4). The terminal diamination proceeds via a stepwise radical mechanism involving Cu(II)[30] intermediate (**B**), and the internal diamination proceeds via a concerted mechanism involving a four-membered Cu(III)[31,32] species (**A**) similar to that of the Pd(0)-catalyzed diamination.[9f] To better understand the Cu(I)-catalyzed diamination,[33,34] we have further investigated this reaction including kinetics, substituent effect, and the effect of different nitrogen sources. Herein, we wish to report our detailed studies on this subject.
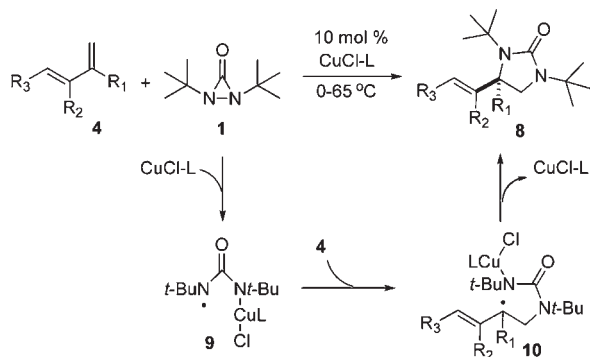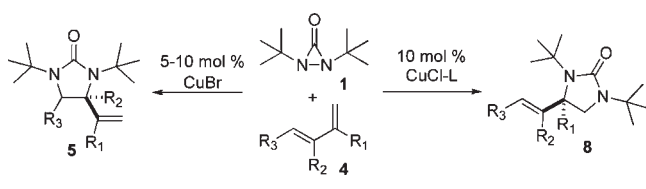
Scheme 1. Pd(0)-Catalyzed Internal Diamination of Dienes
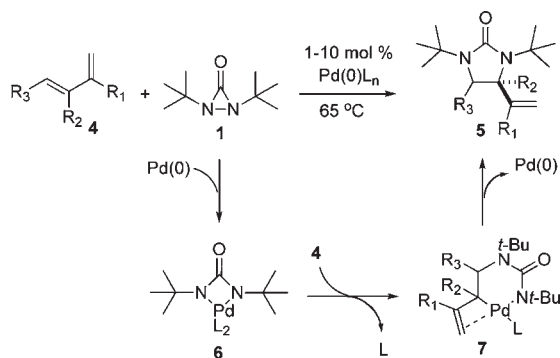
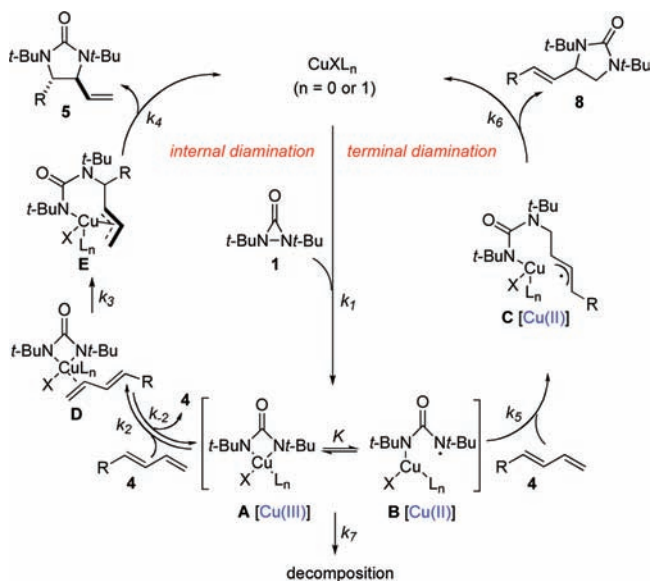**Scheme 2. Cu(I)-Catalyzed Terminal Diamination of Dienes**

Scheme 3. Cu(I)-Catalyzed Regioselective Diamination of Dienes

■ RESULTS AND DISCUSSION

Various conjugated dienes have been investigated for the internal diamination using CuBr[29a] and/or terminal diamination using CuCl-PCy$_3$. As shown in Table 1, 1-monosubstituted (entries 1, 3, and 4), 1,2-disubstituted (entries 7, 8, 10–14), 1,3-disubstituted (entries 15–18), and 1,2,3-trisubstituted (entries 20 and 21) dienes can be efficiently diaminated at the internal double bonds with 5–10 mol % CuBr and N,N-di-t-butyldiaziridinone (1), giving diamination product 5 in good yields and high regioselectivities. 1-Arylbutadienes, such as (E)-1-phenyl-1,3-butadiene, exhibited relatively low regioselectivity for internal diamination using CuBr (Table 1, entry 5) but high regioselectivity for terminal diamination using CuCl-PCy$_3$ (Table 1, entry 6).[35] However, the regioselectivity for the internal diamination using CuBr increased dramatically when additional alkyl substituent(s) were introduced at the 2 and/or 3 positions (Table 1, entries 8, 18, and 21) of the diene substrates. For 1-alkylbutadiene substrates, high regioselectivity can be obtained for either internal

Scheme 4. Proposed Mechanisms for the Cu(I)-Catalyzed Regioselective Diamination of Conjugated Dienes

diamination using CuBr or terminal diamination using CuCl-PCy$_3$ (Table 1, entries 1 and 2).

Kinetic Model and Analysis of the Cu(I)-Catalyzed Regioselective Diamination. Based on the mechanisms proposed in Scheme 4, a kinetic model has been established for the Cu(I)-catalyzed regioselective diamination (for the detailed derivation, see Supporting Information). Using steady-state approximation, the internal diamination and terminal diamination rates are expressed as eqs 1 and 2, respectively. The ratio of internal diamination product 5 to terminal diamination product 8 can be expressed as eq 3, indicating that the diamination regioselectivity is dependent on the equilibrium between A and B (K), the equilibrium between A and D (k_2/k_{-2}), and the rate constants of C–N bond formation (k_3 and k_5):

$$\text{rate}_{\text{internal}} = \frac{k_1 k_2 k_3 [\mathbf{1}][\mathbf{4}][\text{CuXL}_n]}{k_2 k_3 [\mathbf{4}] + K k_{-2} k_5 [\mathbf{4}] + k_{-2} k_7 (1 + K)} \tag{1}$$

$$\text{rate}_{\text{terminal}} = \frac{K k_1 k_{-2} k_5 [\mathbf{1}][\mathbf{4}][\text{CuXL}_n]}{k_2 k_3 [\mathbf{4}] + K k_{-2} k_5 [\mathbf{4}] + k_{-2} k_7 (1 + K)} \tag{2}$$

$$\frac{[\mathbf{5}]}{[\mathbf{8}]} = \frac{k_2 k_3}{K k_{-2} k_5} \tag{3}$$

Kinetic Studies. The proposed diamination mechanism in Scheme 4 involves the cleavage of the N–N bond of N,N-di-t-butyldiaziridinone (1) by the Cu(I) catalyst and the subsequent C–N formation with diene 4. In order to determine the rate-determining step for the reaction, kinetic studies were carried out using 1-methoxy-1,3-butadiene (4c) as substrate for internal diamination (Scheme 5) and (E)-1-phenyl-1,3-butadiene (4d) as substrate for terminal diamination (Scheme 6). The reactions were monitored by ^{1}H NMR spectroscopy using Si(SiMe$_3$)$_4$ as internal standard. The concentrations of diaziridinone 1, internal

**Table 1. Cu(I)-Catalyzed Regioselective Diamination of Dienes**[a]

entry	substrate	method	product	yield (%)[b] (5:8)[c]	entry	substrate	method	product	yield (%)[b] (5:8)[c]
1	4a	A	5a	99	13	4j	A	5j	85
2		B	8a	53 (3:97)	14	4k	A	5k	95 (97:3)[d]
3	4b	A	5b	97 (96:4)	15	4l	A	5l	98
4	4c	A	5c	95	16	4m	A	5m	96 (89:11)
5	4d	A	5d	90 (27:73)	17	4n	A	5n	94
6		B	8d	75	18	4o	A	5o	97 (91:9)
7	4e	A	5e	81	19		B	8o	99
8	4f	A	5f	92 (97:3)	20	4p	A	5p	90
9		B	8f	94	21	4q	A	5q	95
10	4g, n = 1	A	5g-i	95					
11	4h, n = 2			99					
12	4i, n = 3			94					

[a] Method A (taken from ref 29a): All reactions were carried out with olefin **4** (0.20 mmol), N,N-di-t-butyldiaziridinone (**1**) (0.22 mmol), and CuBr (0.010 mmol) in CDCl$_3$ (0.4 mL) under Ar with vigorous stirring at 0 °C for 20 h unless otherwise stated. For entry 3, olefin **4b** (0.19 mmol) was used. For entry 4, olefin **4c** (0.25 mmol, E:Z = 15.7:1, E isomer: 0.24 mmol) and **1** (0.20 mmol) were used. For entry 5, the reaction was carried out with **1** (0.24 mmol), CuBr (0.020 mmol), and CDCl$_3$ (0.8 mL) for 24 h. For entry 12, the reaction was carried out on 0.40 mmol scale. For entry 14, CuBr (0.020 mmol) was used. For entry 18, the reaction was carried out in CDCl$_3$ (1 mL) at −20 °C for 40 h. Method B: All reactions were carried out with olefin **4** (0.20 mmol), **1** (0.40 mmol), CuCl−PCy$_3$ (1:1.5) [0.020 mmol, prepared in situ from CuCl (0.020 mmol) and PCy$_3$ (0.030 mmol) in C$_6$D$_6$ (0.20 mL) by stirring at room temperature for 1 h] in C$_6$D$_6$ (0.25 mL) under Ar at room temperature for 10 h unless otherwise stated. Entries 2 and 19 were taken from ref 29a. For entries 2 and 9, the reactions were carried out with olefin **4** (2.0 mmol) and **1** [0.20 mmol, dissolved in C$_6$D$_6$ (0.1 mL), slow addition over 7 h] at room temperature for 10 h (total). [b] Isolated yield based on **4** except entries 2, 4, and 9 which were based on **1**. [c] The ratio was determined by ^{1}H NMR analysis of the crude reaction mixture. The ratio of **5/8** is >99:1 unless otherwise indicated. For entries 6, 9, and 19, the ratio of **8/5** is >99:1. [d] The stereochemistry was tentatively assigned on the basis of sterics.

diamination product **5c**, and terminal diamination product **8d** were calculated by integration of the signals corresponding to their respective t-butyl groups. As judged by ^{1}H NMR spectroscopy, internal diamination product **5c** and terminal diamination product **8d** were formed with high regioselectivities using 10 mol % CuBr-P(OPh)$_3$ and 10 mol % CuCl-P(OPh)$_3$ as catalysts, respectively.

*Reaction Order in N,N-Di-t-butyldiaziridinone (**1**).* 1-Methoxy-1,3-butadiene (**4c**) was chosen as test substrate for the kinetic studies of internal diamination due to its high reactivity and high regioselectivity for internal diamination. CuBr-P-(OPh)$_3$ (1:1.1) was used as catalyst instead of CuBr (Table 1, method A) for the kinetic study because it was soluble in CDCl$_3$ and also gave the internal diamination product for **4c**. The
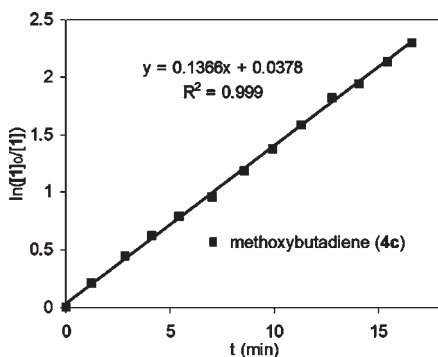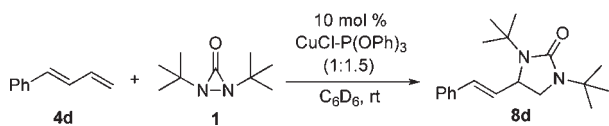
Scheme 5
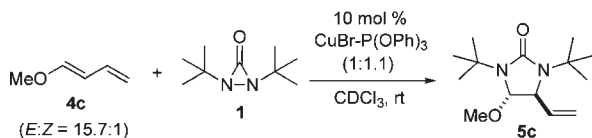
Scheme 6

Figure 1. Plot of $\ln([1]_0/[1])$ against reaction time (min) for the Cu(I)-catalyzed internal diamination of 1-methoxy-1,3-butadiene (**4c**) ($E:Z = 15.7:1$, E isomer: 0.24 mmol) with **1** (0.20 mmol) and CuBr-P(OPh)$_3$ (1:1.1) (0.020 mmol) in CDCl$_3$ (total solution volume: 1.2 mL) in an NMR tube at room temperature. $[1]_0$ stands for the initial concentration of **1** in M, and $[1]$ stands for the concentration of **1** in M at a particular time.
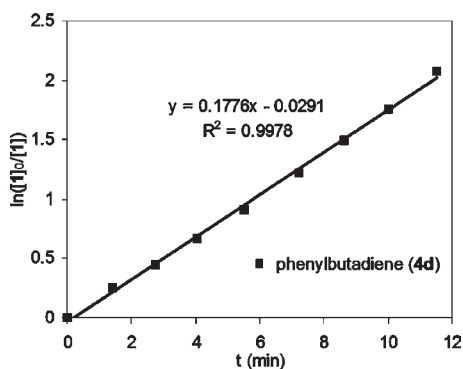

Figure 2. Plot of $\ln([1]_0/[1])$ against reaction time (min) for the Cu(I)-catalyzed terminal diamination of (E)-1-phenyl-1,3-butadiene (**4d**) (0.72 mmol) with **1** (0.20 mmol) and CuCl-P(OPh)$_3$ (1:1.5) (0.020 mmol) in dry C$_6$D$_6$ (total solution volume: 1.2 mL) in an NMR tube at room temperature. $[1]_0$ stands for the initial concentration of **1** in M, and $[1]$ stands for the concentration of **1** in M at a particular time.

reaction was carried out in an NMR tube at room temperature (Scheme 5). Internal diamination product **5c** was cleanly formed during the reaction as judged by ^{1}H NMR
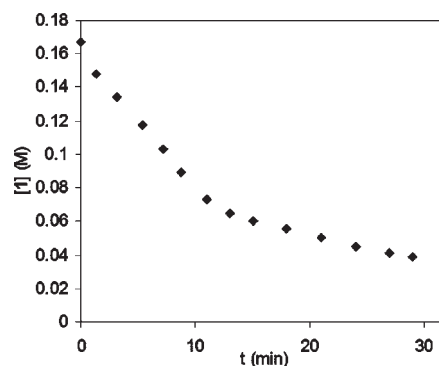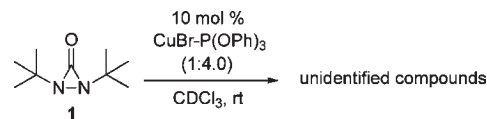
Scheme 7

Figure 3. Plot of $[1]$ against reaction time (min) in the Cu(I)-catalyzed decomposition of N,N-di-t-butyldiaziridinone (**1**) (0.20 mmol) with CuBr-P(OPh)$_3$ (1:4.0) (0.020 mmol) in CDCl$_3$ (total solution volume: 1.2 mL) in an NMR tube at room temperature.
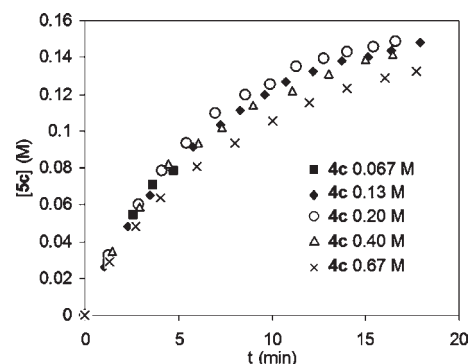

Figure 4. Plots of $[5c]$ (M) against reaction time (min) for the Cu(I)-catalyzed internal diamination of 1-methoxy-1,3-butadiene (**4c**) with variable initial olefin concentrations. The diaminations were carried out with **4c** ($E:Z = 15.7:1$, E isomer: 0.080, 0.16, 0.24, 0.48, or 0.80 mmol), N,N-di-t-butyldiaziridinone (**1**) (0.20 mmol), and CuBr-P(OPh)$_3$ (1:1.1) (0.020 mmol) in CDCl$_3$ (total solution volume: 1.2 mL) in an NMR tube at room temperature.

analysis of the crude reaction mixture. No terminal diamination product and negligible amounts of byproduct from the decomposition of **1** were observed. Since the internal diamination predominates in this case, eq 1 can be simplified to eq 4 (for detailed derivation, see Supporting Information). Equation 4 can be further expressed as eq 5 if the cleavage of the N–N bond of N,N-di-t-butyldiaziridinone (**1**) by the Cu(I) catalyst is the rate-determining step (for detailed derivation, see Supporting Information). The plot of $\ln([1]_0/[1])$ against reaction time gave a straight line with $k_{obs} = 2.3 \times 10^{-3}$ s^{-1} (Figure 1), indicating first-order dependence on diaziridinone **1** in the internal diamination of 1-methoxy-1,3-butadiene (**4c**), which is consistent with the rate law shown in
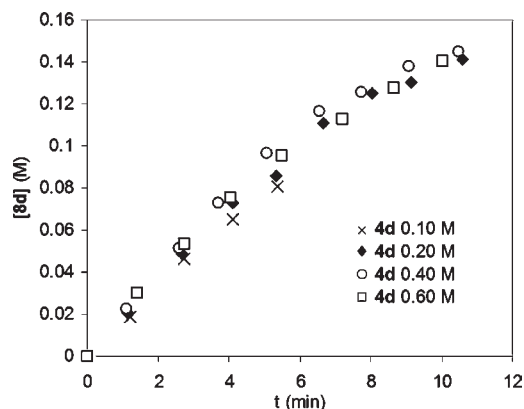
Figure 5. Plots of $[8d]$ (M) against reaction time (min) for the Cu(I)-catalyzed terminal diamination of (*E*)-1-phenyl-1,3-butadiene (**4d**) with variable initial olefin concentrations. The diaminations were carried out with **4d** (0.12, 0.24, 0.48, or 0.72 mmol), *N,N*-di-*t*-butyldiaziridinone (**1**) (0.20 mmol), and CuCl-P(OPh)$_3$ (1:1.5) (0.020 mmol) in C$_6$D$_6$ (total solution volume: 1.2 mL) in an NMR tube at room temperature.
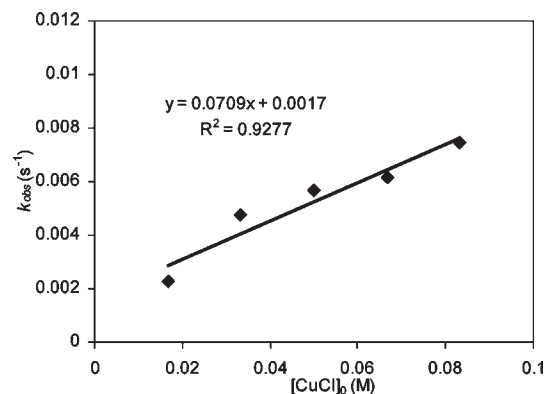

Figure 7. Plot of k_{obs} against $[CuCl]_0$ for the Cu(I)-catalyzed terminal diamination of (*E*)-1-phenyl-1,3-butadiene (**4d**) with variable amounts of total CuCl (0.020−0.10 mmol). The diaminations were carried out with **4d** (0.72 mmol), *N,N*-di-*t*-butyldiaziridinone (**1**) (0.20 mmol), and CuCl-P(OPh)$_3$ (1:1.5) (0.020, 0.040, 0.060, 0.080, and 0.10 mmol) in C$_6$D$_6$ (total solution volume: 1.2 mL) in an NMR tube at room temperature.
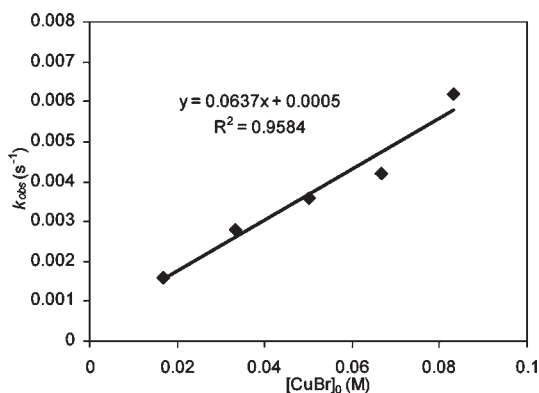

Figure 6. Plot of k_{obs} against $[CuBr]_0$ for the Cu(I)-catalyzed internal diamination of 1-methoxy-1,3-butadiene (**4c**) with variable amounts of total CuBr (0.020−0.10 mmol). The diaminations were carried out with **4c** (*E:Z* = 15.7:1, *E* isomer: 0.24 mmol), *N,N*-di-*t*-butyldiaziridinone (**1**) (0.20 mmol), and CuBr-P(OPh)$_3$ (1:1.1) (0.020, 0.040, 0.060, 0.080, and 0.10 mmol) in CDCl$_3$ (total solution volume: 1.2 mL) in an NMR tube at room temperature.

Figure 8. EPR spectrum for the reaction between *N,N*-di-*t*-butyldiaziridinone (**1**) (0.050 mmol) and CuCl-P(OPh)$_3$ (1:1.5) (0.0050 mmol) in toluene (0.18 mL) at −50 °C. A similar triplet was also observed when the reaction was performed in the presence of (*E*)-1-phenyl-1,3-butadiene **4d** (0.10 mmol).

eq 5:

$$\text{rate}_{\text{internal}} = k_1[\mathbf{1}][\text{CuXL}_n] \quad (4)$$

$$\text{rate}_{\text{internal}} = k_1[\mathbf{1}][\text{CuXL}_n]_0 \quad (5)$$

The diamination of 1-phenyl-1,3-butadiene (**4d**) with 10 mol % CuCl-P(OPh)$_3$ and **1** occurred regioselectively at the terminal double bond as judged by the ^{1}H NMR of the crude reaction mixture. CuCl-P(OPh)$_3$ was chosen as catalyst instead of CuCl-PCy$_3$ (Table 1, method B) for the kinetic study because the ^{1}H NMR signal of P(OPh)$_3$ does not interfere with the signals of the *tert*-butyl groups of **1** and **8d** as PCy$_3$ does. Equation 2 can be similarly simplified to eq 6 if the cleavage of the N−N bond of *N,N*-di-*t*-butyldiaziridinone (**1**) is also assumed to be the rate-determining step. The straight line obtained for the plot of $\ln([\mathbf{1}]_0/[\mathbf{1}])$ against reaction time with $k_{obs} = 3.0 \times 10^{-3} \text{ s}^{-1}$ (Figure 2) also
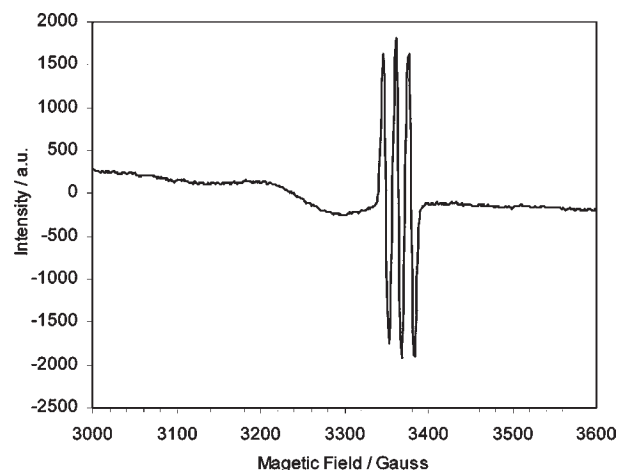
indicates first-order kinetics in *N,N*-di-*t*-butyldiaziridinone (**1**) in this case:

$$\text{rate}_{\text{terminal}} = k_1[\mathbf{1}][\text{CuXL}_n]_0 \quad (6)$$

The decomposition of *N,N*-di-*t*-butyldiaziridinone (**1**) was investigated using CuBr-P(OPh)$_3$ (1:4) complex as catalyst in the absence of a diene substrate (Scheme 7). The reaction was carried out in CDCl$_3$ and monitored by ^{1}H NMR spectroscopy. *N,N*-di-*t*-butyldiaziridinone (**1**) rapidly decomposed to unidentified compounds (Figure 3). Under the reaction conditions, Cu species **A** or **B** cannot be detected by NMR spectroscopy even with stoichiometric amounts of Cu(I) salt at low temperature, which indicates the decomposition of **A** and **B** should be faster than their formation. Under the diamination conditions, the reaction between **A** and **B** with the diene substrate should be even

Table 2. Studies of the Effect of Copper Salt on the Diamination of (E)-Nona-1,3-diene (4b)[a]
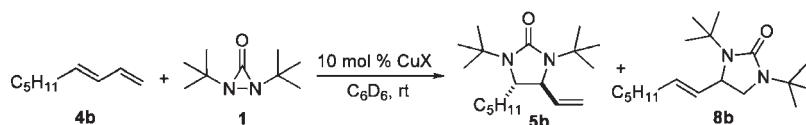
entry	catalyst	conv. (%)[b]	5b:8b[c]
1	CuCl-P(OPh)$_3$	60	0.37:1
2	CuBr-P(OPh)$_3$	69	1.26:1
3	CuI−P(OPh)$_3$	29	0.11:1
4	CuOAc-P(OPh)$_3$	0	
5	CuCN-P(OPh)$_3$	50	0:1
6	CuSPh-P(OPh)$_3$	0	

[a] The diamination was carried out with diene **4b** (0.20 mmol), N,N-di-t-butyldiaziridinone (**1**) (0.30 mmol), and CuX-P(OPh)$_3$ (1:1.5) (0.020 mmol) in C$_6$D$_6$ (0.20 mL) in a 1.5 mL vial at room temperature under Ar for 10 h unless otherwise stated. [b] The conversion was based on diene **4b** and determined by ^{1}H NMR analysis of the crude reaction mixture. [c] The ratio of **5b:8b** was determined by ^{1}H NMR analysis of the crude reaction mixture except for entry 3. For entry 3, an accurate ratio of **5b** to **8b** was difficult to obtain by ^{1}H NMR analysis of the crude reaction mixture due to the signal interference with baseline noise and unknown byproducts. The ratio was thus obtained by ^{1}H NMR analysis after flash chromatography (**5b** and **8b** were nearly inseparable by column).

Table 3. Studies of the Ligand Effect on the Cu(I)-Catalyzed Diamination of (E)-Nona-1,3-diene (4b)[a]
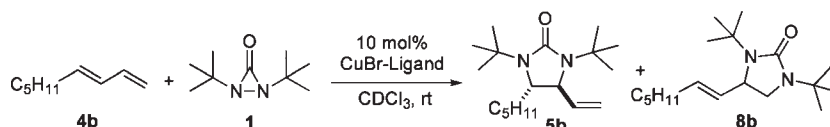
| entry	ligand (L:Cu)	conv. (%)[b]	5b:8b[c]
1	(±)-BINAP(1.5:1)	0	
2	PPh$_3$ (1.5:1)	72	0.76:1
3	P(4-MeOPh)$_3$ (1.5:1)	60	0.35:1
4	P(4-CF$_3$Ph)$_3$ (1.5:1)	92	1.59:1
5	P(cyclohexyl)$_3$ (1.5:1)	77	0.33:1
6	P(OPh)$_3$ (1:1)	99	2.9:1
7	P(OPh)$_3$ (1.5:1)	94	1.89:1
8	P(OPh)$_3$ (4:1)	87	0.92:1
9	no ligand	99	10:1

[a] The diaminations were carried out with diene **4b** (0.20 mmol), N,N-di-t-butyldiaziridinone (**1**) (0.30 mmol), and CuBr-ligand (0.020 mmol) in CDCl$_3$ (0.2 mL) in a 1.5 mL vial at room temperature under Ar for 10 h. [b] The conversion was based on diene **4b** and determined by analysis of the ^{1}H NMR spectrum of the crude reaction mixture. [c] The ratio of **5b:8b** was determined by ^{1}H NMR analysis of the crude reaction mixture.

faster than the decomposition of **A** and **B**, which also suggests the formation of **A** and **B** is likely to be the rate-determining step.

Effect of Olefin Concentration. According to eqs 5 and 6, the internal and terminal diamination reactions should be zero order in olefin **4**. The effect of olefin concentration on the internal and the terminal diaminations was investigated using 1-methoxy-1,3-butadiene (**4c**) and (E)-1-phenyl-1,3-butadiene (**4d**), respectively. Similar reaction rates were observed for the CuBr-catalyzed internal diamination when $[4c]_0$ varied from 0.067 to 0.40 M (Figure 4). The slightly reduced reaction rate observed with high $[4c]_0$ (0.67 M) is possibly due to the complexation of the Cu catalyst with the diene substrate. For the CuCl-catalyzed terminal diamination of (E)-1-phenyl-1,3-butadiene (**4d**), similar reaction rates were also observed when $[4d]_0$ varied from 0.10 to 0.60 M (Figure 5). These results indicate that the potential involvement of copper-diene complexes has little affect on the overall kinetic profile, and the concentration of diene **4c** or **4d** has negligible

influence on the rate of diamination, which is consistent with the rate law as expressed in eqs 5 and 6. The fact that the diamination is first order in N,N-di-t-butyldiaziridinone (**1**) (Figures 1 and 2) and zero order in diene **4** (Figures 4 and 5) further indicates that the cleavage of the N−N bond of **1** by the Cu(I) complex to form active Cu species **A** and **B** is the rate-determining step of the diamination.

Effect of Total Cu Concentration. According to eqs 5 and 6, the internal and terminal diaminations should be first order in total Cu catalyst concentration. CuBr-catalyzed internal diamination of 1-methoxy-1,3-butadiene (**4c**) and CuCl-catalyzed terminal diamination of (E)-1-phenyl-1,3-butadiene (**4d**) were then investigated with variable amounts of initial Cu salts. The plots of k_{obs} against total Cu catalysts ($[CuBr]_0$ and $[CuCl]_0$) have found to be straight lines, as shown in Figure 6 for the internal diamination of **4c** and in Figure 7 for the terminal diamination of **4d**. This data indicate that the internal and terminal diaminations are first order in total Cu catalyst as expressed in eqs 5 and 6.

Table 4. Competition Experiments of CuCl-Catalyzed Terminal Diamination of para-Substituted (E)-1-phenyl-1,3-butadienes 4[a]
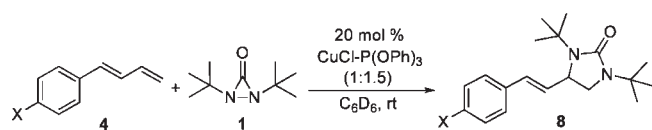
entry	arylbutadiene (4)	ratio of $[8]_x/[8]_H$[b]
1	X = Me, **4r**	1.18
2	X = Ph, **4s**	1.33
3	X = H, **4d**	1.00
4	X = Cl, **4t**	1.13
5	X = Br, **4u**	1.08
6	X = NO$_2$, **4v**	1.55

[a] The competitive diaminations were carried out with **4d** (1.0 mmol), competing diene (**4r**, **4s**, **4t**, **4u**, or **4v**) (1.0 mmol), N,N-di-t-butyldiaziridinone (**1**) (0.10 mmol), and CuCl-P(OPh)$_3$ (1:1.5) (0.020 mmol) in C$_6$D$_6$ (1.0 mL) in a 3.0 mL vial under Ar at room temperature for 6 h. [b] The ratio of $[8]_x/[8]_H$ was determined by ^{1}H NMR analysis of the crude reaction mixture.
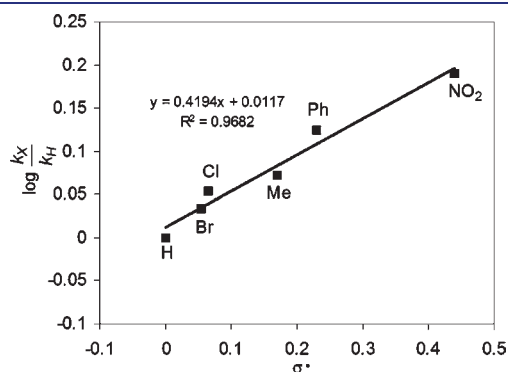
EPR Studies. Intermediates **A** and **B** are proposed to be involved in the Cu(I)-catalyzed diamination with N,N-di-t-butyldiaziridinone (**1**) (Scheme 4). However, these intermediates could not be detected by the NMR spectroscopy. Electron paramagnetic resonance (EPR) spectroscopy was subsequently used to detect any radical species. A triplet with a 1:1:1 intensity ratio was observed when N,N-di-t-butyldiaziridinone (**1**) was treated with CuCl-P(OPh)$_3$ (1:1.5) at low temperature (Figure 8), which supports the existence of nitrogen radical intermediate **B**.

Effect of Copper Salt and Ligand. The effect of copper salt on the diamination was investigated in C$_6$D$_6$ using (E)-nona-1,3-diene (**4b**) as substrate (Table 2). CuCl and CuBr exhibited the highest catalytic activity for the diamination (Table 2, entries 1 and 2). CuBr gave the highest regioselectivity for the internal diamination (Table 2, entry 2). Interestingly, CuCN gave only terminal diamination product with moderate catalytic activity (Table 2, entry 5). Apparently, the counteranion of the Cu(I) salt has a dramatic effect on the reactivity and selectivity for the diamination. The counteranion could affect the reaction by altering the relative stability and/or reactivity of four-membered Cu(III) species **A** and Cu(II) radical species **B**.
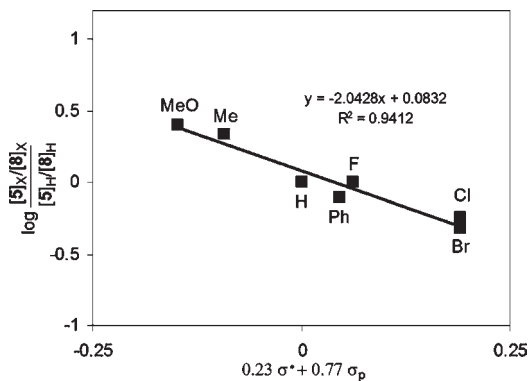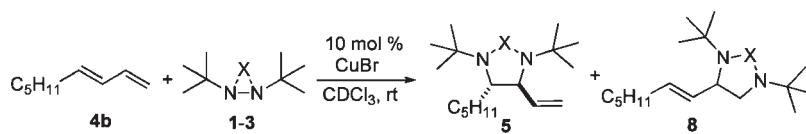

Figure 9. Plot of $\log(k_X/k_H)$ against radical substituent constant $\sigma^\bullet$ for the CuCl-catalyzed terminal diamination of para-substituted (E)-1-phenyl-1,3-butadienes **4**. The radical substituent constants $\sigma^\bullet$ were taken from ref 36b.
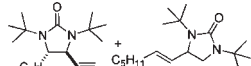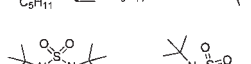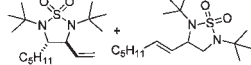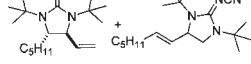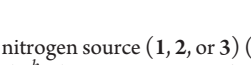
Figure 10. Hammett correlation of regioselectivity ($[5]/[8]$) for the CuBr-catalyzed diamination of para-substituted (E)-1-phenyl-1,3-butadienes **4**. The radical substituent constants $\sigma^\bullet$ were taken from ref 36b, and the substituent constants σ_p were taken from ref 38.

Table 5. Ratio of $[5]/[8]$ for the CuBr-Catalyzed Diamination of para-Substituted (E)-1-Phenyl-1,3-butadienes 4[a]
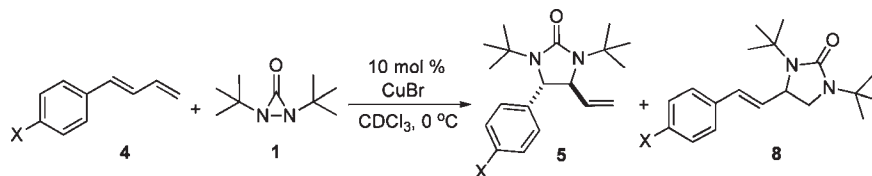
entry	arylbutadiene (4)	$[5]/[8]$[b]
1	X = OMe, **4w**	0.94
2	X = Me, **4r**	0.80
3	X = Ph, **4s**	0.29
4	X = H, **4d**	0.37
5	X = F, **4x**	0.37
6	X = Cl, **4t**	0.21
7	X = Br, **4u**	0.18

[a] The diamination was carried out with diene **4** (0.20 mmol), N,N-di-t-butyldiaziridinone (**1**) (0.24 mmol), and CuBr (0.020 mmol) in CDCl$_3$ (0.80 mL) in a 1.5 mL vial at 0 °C under Ar for 24 h. [b] The ratio of $[5]/[8]$ was determined by ^{1}H NMR analysis of the crude reaction mixture.

Table 6. CuBr-Catalyzed Diamination of (E)-Nona-1,3-diene (4b) with Nitrogen Sources 1−3[a]

entry	nitrogen source	products	conv. (%)[b]	[5]/[8][c]
1	**1**		> 99	11:1
2	**2**		87	6.8:1
3	**3**		44	<1:99

[a] The diamination was carried out with diene **4b** (0.20 mmol), nitrogen source (**1**, **2**, or **3**) (0.30 mmol), and CuBr (0.020 mmol) in CDCl$_3$ (0.4 mL) in a 1.5 mL vial at room temperature under Ar atmosphere for 20 h. [b] The conversion was based on diene **4b** and determined by ^{1}H NMR analysis of the crude reaction mixture. [c] The ratio of [5]:[8] was determined by ^{1}H NMR analysis of the crude reaction mixture.

Various ligands were also investigated for the Cu(I)-catalyzed diamination of (E)-nona-1,3-diene (**4b**) (Table 3). Bidentate phosphine, such as BINAP, was found to be an ineffective ligand for the diamination (Table 3, entry 1). Monodentate ligands exhibited good activity for the reaction (Table 3, entries 2−8). The regioselectivity was also greatly influenced by the ligand. It appears that electron-rich ligands, such as tris(4-methoxyphenyl)-phosphine and tricyclohexylphosphine, favored terminal diamination (Table 3, entries 3 and 5), whereas electron-deficient ligands, such as tris(4-trifluoromethylphenyl)phosphine, favored internal diamination (Table 3, entry 4). The Cu−ligand ratio was also investigated. Increasing the amount of ligand lowered the regioselectivity for internal diamination product (Table 3, entries 6−8). CuBr without ligand gave the highest regioselectivity for internal diamination (Table 3, entry 9). The ligand could influence the relative amount and/or reactivity of four-membered Cu(III) species **A** and Cu(II) radical species **B**, consequently affecting the regioselectivity of the diamination. Coordination of a ligand (particularly a bulky ligand such as PCy$_3$) to the Cu could increase the steric congestion around the Cu and cause the equilibrium to shift toward the sterically less crowded Cu(II) radical species **B**, favoring terminal diamination. At the same time, coordination of a ligand to the Cu could disfavor the formation of complex **D** and subsequent internal diamination.

Substituent Effect. The diamination of various para-substituted (E)-1-phenyl-1,3-butadienes was carried out using CuCl-P-(OPh)$_3$ (1:1.5) in C$_6$D$_6$. Under these reaction conditions, the diamination occurred essentially only at the terminal double bond, as judged by ^{1}H NMR spectroscopy. As shown in Table 4, the diamination was accelerated by both electron-donating and electron-withdrawing substituents (Table 4, entries 1, 2, 4−6 vs entry 3). The Hammett plot of $\log(k_X/k_H)$ against radical substituent constant $\sigma^\bullet$ for the reaction gave a straight line as shown in Figure 9,[36,37] which is consistent with the radical mechanism proposed for the terminal diamination, as shown in Scheme 4 [for the Hammett plot of $\log(k_X/k_H)$ against σ_p, see: Figure 9a in Supporting Information].

Scheme 8

The diamination of para-substituted (E)-1-phenyl-1,3-buta-dienes was also carried out with 10 mol % CuBr as catalyst. Under these reaction conditions, a mixture of internal and terminal diamination products (**5** and **8**) was formed. As shown in Table 5, in all these cases the terminal diamination product (**8**) was the major product. However, the relative amount of internal diamination product increased with the electron-donating capability of the substituents. A good correlation was obtained in th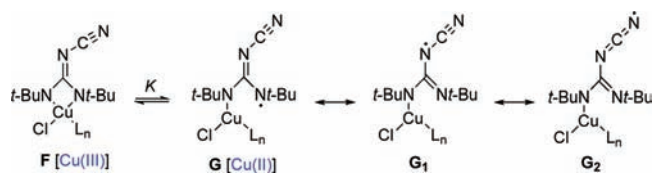e Hammett plot of the regioselectivity ([5]/[8]) against $0.23\sigma^\bullet + 0.77\sigma_p$ (Figure 10) using the best-fit approach (for the Hammett plots of the regioselectivity against $\sigma^\bullet$ and σ_p, see: Figures 10a and 10b in Supporting Information).[36−38] The regioselectivity of the diamination appears to be more sensitive to substituent constant σ_p (77%) than to radical-based substituent constant $\sigma^\bullet$. The negative slope suggests that radical-stabilizing and electron-withdrawing substituents decrease the ratio of internal to terminal diamination ([5]/[8]) and that the internal diamination of diene **4** with Cu(III) species **A** (Scheme 4) is likely to be electrophilic in nature.

Effect of Nitrogen Source. The diamination of (E)-nona-1,3-diene (**4b**) was investigated with 10 mol % CuBr as catalyst using different nitrogen sources (**1**, **2**, and **3**). These three nitrogen sources displayed very different regioselectivity in the diamination reaction. While N,N-di-t-butyldiaziridinone (**1**) gave high regioselectivity favoring internal diamination (Table 6, entry 1), N,N-di-t-butyl-3-(cyanimino)-diaziridine (**3**) afforded essentially only the terminal diamination product (Table 6, entry 3). The high regioselectivity for terminal diamination exhibited by **3** is likely due to the fact that the CN group can stabilize the radical Cu(II)

species **G**, thus steering the reaction toward the terminal diamination (Scheme 8). At the same time, higher content of radical species **G** likely leads to more rapid decomposition of **3** via the radical pathway, thus giving relatively lower conversion for the diamination (44%).

■ CONCLUSION

Mechanistic studies have shown that the Cu(I)-catalyzed diamination of conjugated dienes proceeds via two distinct mechanistic pathways (Scheme 4). The reaction begins with the cleavage of the N—N bond of *N,N*-di-*t*-butyldiaziridinone (**1**) by the Cu(I) catalyst to form four-membered Cu(III) species **A** and Cu(II) radical species **B**, which are in rapid equilibrium. For the internal diamination, Cu(III) species **A** coordinates with conjugated diene **4** to form olefin-Cu complex **D**, which undergoes migratory insertion and subsequent reductive elimination to form internal diamination product **5** and regenerates the Cu(I) catalyst. For the terminal diamination, nitrogen radical **B** adds to the terminal double bond of conjugated diene **4** to form Cu(II) allyl radical species **C**, which undergoes the subsequent C—N bond formation to give terminal diamination product **8** and regenerates the Cu(I) catalyst. The existence of nitrogen radical intermediate **B** was supported by EPR spectroscopy.

Kinetic studies have shown that the diamination is first order in *N,N*-di-*t*-butyldiaziridinone (**1**), zero order in olefin, and first order in total Cu(I) catalyst, suggesting that the cleavage of the N—N bond of **1** by the Cu(I) catalyst is the rate-determining step. Studies with para-substituted 1-phenyl-1,3-butadienes have shown that the Cu(I)-catalyzed terminal diamination was favored by both electron-donating and electron-withdrawing substituents. A good correlation of the Hammett plot with radical-based substituent constants $\sigma^{\bullet}$ supports the proposed radical mechanism for the terminal diamination. The CuBr-catalyzed diamination of para-substituted 1-phenyl-1,3-butadienes afforded a mixture of terminal and internal diamination products (**5** and **8**). The regioselectivity ([**5**]/[**8**]) had a good Hammett correlation with $0.23\sigma^{\bullet} + 0.77\sigma_{\mathrm{p}}$ (Figure 10), suggesting the substituent constant σ_{p} contributes more to regioselectivity than the radical-based substituent constant $\sigma^{\bullet}$ does. The negative slope indicates that the internal diamination with Cu(III) intermediate **A** is electrophilic. Conjugated dienes with good radical-stabilizing groups, such as 1-aryl-1,3-butadienes, are effective substrates for terminal diamination. Electron-rich dienes favor the internal diamination. Besides diene substrates, the competition between the terminal and internal diamination is also dependent upon reaction conditions, such as Cu(I) catalyst and ligand[29] as well as the nitrogen source. *N,N*-di-*t*-butyldiaziridinone (**1**) is the most regioselective nitrogen source for the CuBr-catalyzed internal diamination of conjugated dienes, and *N,N*-di-*t*-butyl-3-(cyanimino)-diaziridine (**3**) exhibits the highest regioselectivity for terminal diamination.

The current mechanistic studies have shown that Cu(III) and Cu(II) species can coexist in rapid equilibrium in the catalytic cycle of the diamination. The Cu(III) species accounts for a concerted reaction pathway leading to internal diamination, whereas the Cu(II) species accounts for a radical reaction pathway leading to terminal diamination. The extent of the involvement of the Cu(III) or Cu(II) species depends upon reaction conditions and substrates used.

■ ASSOCIATED CONTENT

⑤ Supporting Information. Procedures for diamination, kinetic studies, EPR study, studies of substituent effect and nitrogen

sources, and characterization data along with NMR spectra. This material is available free of charge via the Internet at http://pubs. acs.org.

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