Use of Cyclopropane as C1 Synthetic Unit by Directed Retro-Cyclopropanation with Ethylene Release

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ABSTRACT: Cyclopropanation of alkenes is a well-established textbook reaction for the synthesis of cyclopropanes, where "high-energy" carbene species is exploited for driving the reaction forward. However, little attention has been paid to molecular transformations involving the reverse reaction, retro-cyclopropanation (RC). This is because of difficulties associated with both cleaving the two geminal C–C single bonds and exploiting the generated carbenes for further transformations in an efficient and selective manner. Here we report that a molybdenum-based catalytic system overcomes the above challenges and effects the RC of cyclopropanes bearing a pyridyl group with the release of ethylene (alkene) and the subsequent intramolecular cyclization leading to pyrido[2,1-*a*]isoindoles. The reaction allows for the uncommon use of cyclopropanes as C1 synthetic units in contrast to most conventional reactions in which cyclopropanes are used as C3 synthetic units. We anticipate that this new strategy will pave the way for C1 cyclopropane chemistry.

INTRODUCTION

Cyclopropanes are three-membered carbocycles that display unique properties and reactivities because of their unusual bonding and ring strain. Ubiquitous in naturally occurring compounds and rationally designed drugs, cyclopropane-containing molecules themselves are important,[1,2,3,4,5,6,7,8] but they also serve as versatile synthetic intermediates in modern organic synthesis.[8,9,10,11,12,13,14,15] Certain transition metals are capable of cleaving the C–C bond via oxidative addition to form metallacyclobutane intermediates with strain release (ca. 27 kcal/mol) as a driving force (Fig. 1a, top).[16,17,18,19] Synthetic chemists have successfully utilized the key intermediates, mostly as C3 fragments for various transformations such as addition, cycloaddition, and cycloisomerization reactions, wherein activated cyclopropanes such as donor–acceptor cyclopropanes,[20] vinylcyclopropanes,[21] and alkylidenecyclopropanes[22] are often employed to facilitate the C–C bond cleavage step.

If the metallacyclobutane intermediate further undergoes the second cleavage of a C–C bond, a metal carbene species is formed with the release of ethylene, a common step involved in the olefin metathesis reaction (Fig. 1a, bottom). The overall sequence is retro-cyclopropanation (RC), i.e., fragmentation of a cyclopropane into an ethylene and a carbene species. This is a highly uphill and difficult process unless appropriate stabilization of the generated metal carbene is exerted. Indeed, the generation of metal carbene largely relies on the cleavage of the weak bonds in "high-energy" compounds such as diazo compounds, frequently used but potentially explosive carbene precursors, and the metal carbene generation by breaking the two C–C bonds of stable cyclopropanes remains challenging.[23] Because of the lack of efficient and selective catalytic systems that can achieve both RC and subsequent transformation of metal carbenes, such reactions that use cyclopropanes as C1 synthetic units have scarcely been reported. In this context, the biosynthesis of ethylene, a natural plant hormone, by oxidative fragmentation of 1-aminocyclopropane-1-carboxylic acid with concomitant release of HCN (C1 unit) and CO_2 may be relevant but lacks the intermediacy of a carbene species.[24,25]

Cationic gold(I) can promote the retro-Buchner reaction, a special case of RC, where a substituted methylene moiety is removed from 1,3,5-cycloheptatriene, which is in equilibrium with norcaradiene, with the release of benzene (Fig. 1b).[26] The intramolecular RC of bicyclo[1.1.0]butane is proposed to be involved under transition-metal catalysis, such as Ni[27] and Rh[28] (Fig. 1c). These reactions take advantage of aromatization and the release of extremely high ring strain (63–67 kcal/mol)[18,19] as driving force. However, the substrates are then limited to highly strained cyclopropanes. The intermolecular RC was observed in the Rh(I)-catalyzed [2+2+1]

cycloaddition reaction of alkylidenecyclopropanes[29] and the Rh(I)-catalyzed [5+2–2] cycloisomerization-type reaction of allenylcyclopropanes.[30] However, the former reaction still relies on the higher ring strain of alkylidenecyclopropanes (38–41 kcal/mol)[18,19] and requires slow addition of diynes to suppress side reactions following non-RC paths in some cases, and the latter reaction suffers from low selectivity between the cycloisomerizations with and without ethylene release (Fig. 1d and 1e). The $PhWCl_3/RAlCl_2$ binary system was found to catalyze RC of simple cyclopropanes[31] and cyclopropane–olefin metathesis,[32] albeit again with low efficiency (Fig. 1f).[33]

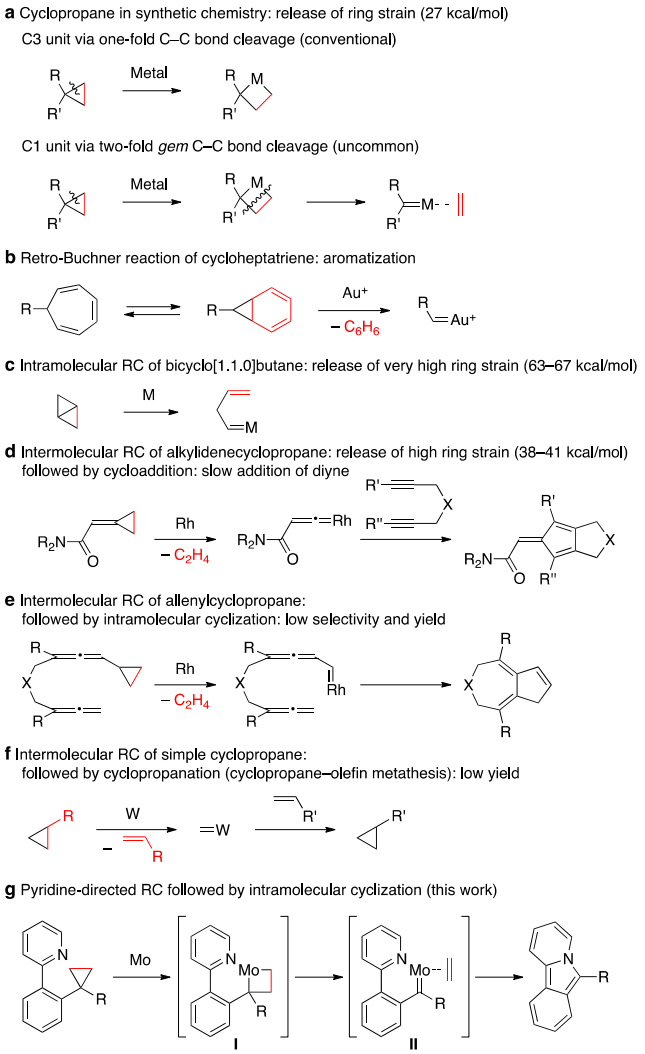

Figure 1. Organic transformations involving retro-cyclopropanation with metal catalysts.

Thus, to date, few efficient catalytic systems are available for molecular transformations featuring RC with synthetic utility. Here we describe a molybdenum-catalyzed directed RC/intramolecular cyclization sequence of cyclopropanes possessing a pyridine moiety that plays multiple roles (Fig. 1g). With the prevalence of the chelation assistance in the activation of chemically inert bonds, such as C–H and C–C bonds, together with our own experience in this field,[34,35] we envisioned that the use of a pyridyl group at an appropriate position for RC would be beneficial for the following reasons: it would 1) facilitate the first cleavage of a proximal C–C bond in a regioselective manner, 2) prohibit the undesired decomposition of the metallacyclobutane intermediate **I** through a hydride elimination process,[36] 3) adequately stabilize the carbene species **II** formed after the elimination of ethylene from **I**, and 4) efficiently trap the carbene by intramolecular cyclization to incorporate itself into the value-added product. The directing group approaches for the regioselective transformations of cyclopropanes have been reported.[37] However, the cyclopropanes are still used as C3 synthetic units in these cases, because the C–C bond cleavage takes place only once.

RESULTS AND DISCUSSION

To test this hypothesis, we commenced our investigation using 2-[2-(1-phenylcyclopropyl)phenyl]pyridine (**1a**) as a model substrate (Fig. 2). Close similarity between the proposed mechanism in our strategy (Fig. 1g) and that of the olefin metathesis, significant advances of which have been made with molybdenum catalysts[38,39] besides our recent interest in molybdenum catalysis[40,41] prompted us to use this metal as a catalyst of choice; hence we first explored various combinations of molybdenum complexes and ligands. After extensive experimentation, we found that a catalytic amount of $Mo(benzene)_2$ combined with 9,10-phenanthrenequinone (**L1**) effectively catalyzed the RC/intramolecular cyclization reactions to afford 6-phenyl[2,1-*a*]pyridoisoindole (**2a**) in quantitative yield. The reaction reached completion with 20 mol % catalyst after 24 h at 160 °C in mesitylene, whereas at lower temperatures the reaction rate was significantly decreased (Table S1), partly because the thermodynamic driving force of releasing ethylene decreases as the temperature decreases (ΔG = –3.7, –2.3, and +1.1 kcal/mol, at 160, 120, and 25 °C, respectively). The reaction still proceeded with 10 mol % catalyst loading, but with slower reaction rates (Table S1).

Screening of various ligands revealed that *o*-quinones were uniquely effective in the reaction; **L1** and **L2** performed best (Fig. 2a). While catechol showed similar catalytic activity (**L3**), common bidentate nitrogen- or phosphine-based ligands completely shut off the reaction (**L4**–**L7**). $Mo(benzene)_2$ alone could effect the reaction to some extent, but the reaction in the absence of molybdenum did not proceed at all. Other Mo(0) complexes such as $Mo(CO)_6$ and $Mo(CO)_3(MeCN)_3$ also worked, but less efficiently (Table S2).

The scope of the directed RC reaction is illustrated in Fig. 2b. Cyclopropanes possessing an electron-rich and electron-deficient aryl group at the 1-position of the cyclopropane both reacted smoothly (**2b**–**2g**). Cyclopropanes with a bulky 2-tolyl or alkyl substituents were less reactive but they still underwent the RC reactions at higher temperature and after longer reaction time (**2h**–**2k**). Due to the moderate instability of 6-alkylpyrido[2,1-*a*]isoindoles (**2i**–**2k**) under atmospheric conditions, these products were oxidized and then isolated as the corresponding alkyl 2-(2-pyridyl)phenyl ketones. 2-(2-Cyclopropylphenyl)pyridine remained unchanged, indicating the necessary presence of a substituent at the 1-position of the cyclopropane. Both an electron donating and withdrawing substituent on the 2-phenylpyridine moiety slowed down the reaction (**2m** and **2n**). In addition to a pyridyl group, a pyrimidyl group also worked as a multifunctional unit and the corresponding pyrimido[2,1-*a*]isoindole (**2o**) was obtained in good yield, whereas an imino group failed to effect the reaction. All the 6-arylpyrido[2,1-*a*]isoindole derivatives synthesized by this method are previously unknown compounds, and exhibit strong fluorescence.[42]

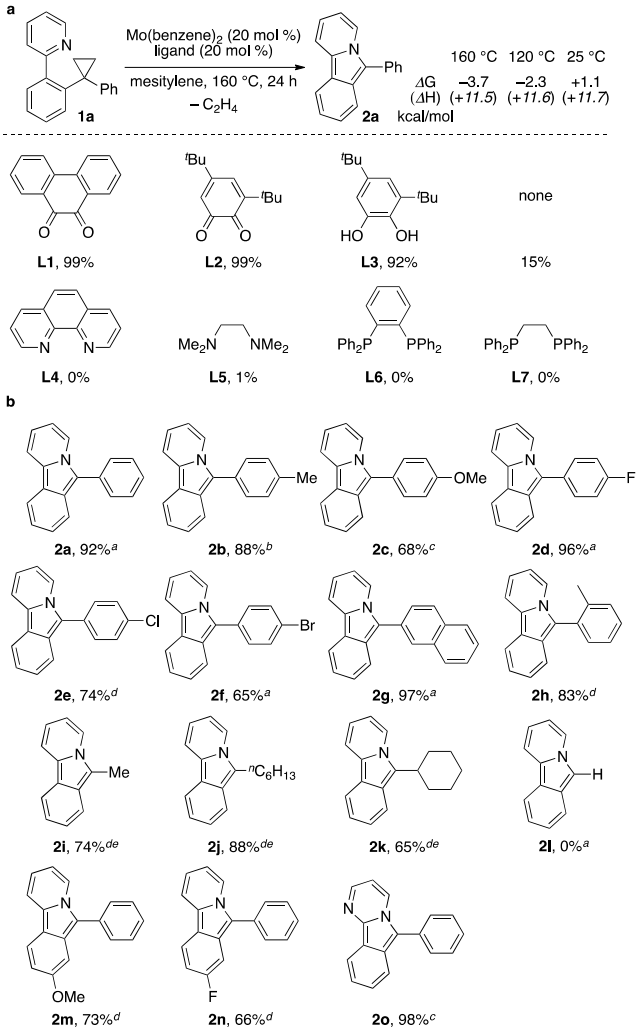

Figure 2. **Molybdenum-catalyzed synthesis of pyrido[2,1-*a*]isoindoles via retro-cyclopropanation**. **a**, Gibbs free energies and enthalpies of the reaction calculated at the M06/6-31G(d,p)$_{\text{mesitylene(SMD)}}$ level of theory and the effects of ligands. ^{1}H NMR yields are shown. **b**, Scope of the molybdenum-catalyzed RC. The reactions were performed on a 0.2 mmol scale with Mo(benezene)$_2$/**L1** (20 mol%) in mesitylene (0.25 M). Isolated yields are shown. [a]160 °C, 24 h. [b]160 °C, 18 h. [c]180 °C, 24 h. [d]180 °C, 72 h. [e]Isolated as ketone after oxidation. Ph, phenyl; ^{t}Bu, *tert*-butyl; Me, methyl.

The importance of a pyridyl directing group for the molybdenum-catalyzed RC was illustrated by the reaction of 2-(1-phenylcyclopropyl)-1,1'-biphenyl. It did not afford any products with ethylene loss or ring-opened products both in the presence and absence of added pyridine (Fig. 3a). Monitoring the reaction in *p*-xylene-d_{10} in an NMR tube confirmed the evolution of ethylene, observed in 26% ^{1}H NMR yield after 24 h at 160 °C and in 31% yield after leaving the resulting mixture at ambient temperature for another day (Fig. 3b). Results of the RC with 2-substituted cyclopropanes also confirmed the liberation of alkene. Thus, a cyclopropane possessing a *cis*-decyl substituent at the 2-position (**3**$_{cis}$) was cleanly converted to **2a** in 87% yield with dodecenes detected in 87% total yield (Fig. 3c). Similarly, a cyclopropane with a *trans*-decyl substituent (**3**$_{trans}$) afforded **2a** in 57% yield with dodecenes detected in 54% total yield.

The proposed mechanism commences with coordination of a pyridyl group to the active molybdenum species generated in situ from Mo(0) and *o*-quinone (Fig. 3d). The regioselective cleavage of the proximal C–C bond of the cyclopropane ring affords the molybdenacyclobutane intermediate (**I**), which undergoes a second cleavage of the C–C bond with release of ethylene to form the molybdenum carbene species (**II**). The C–N bond forming intramolecular cyclization finally yields the pyridoisoindole product and regenerates the active species.

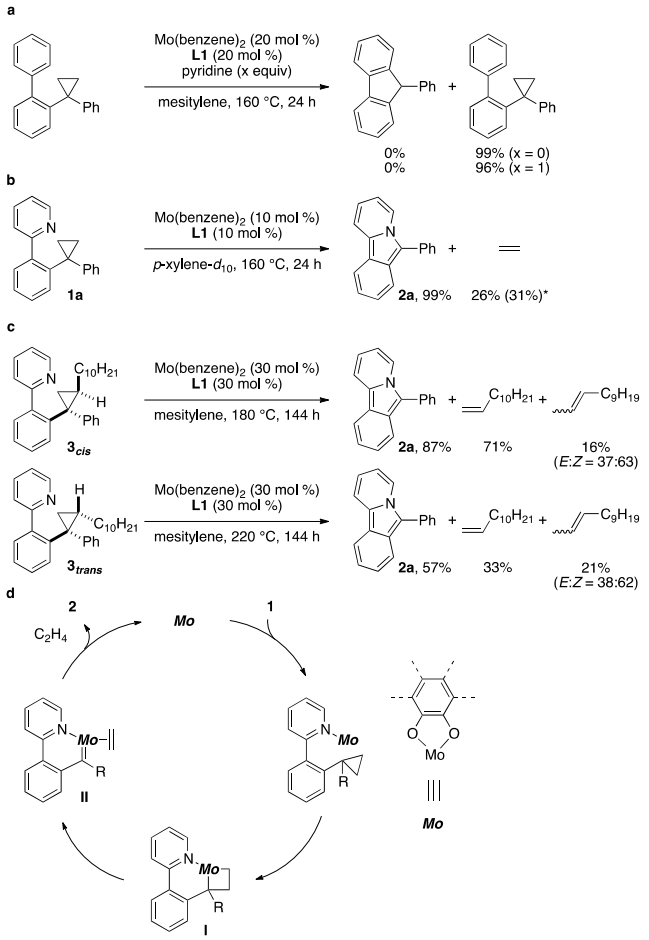

Figure 3. Molybdenum-catalyzed retro-cyclopropanation with release of alkene and the proposed mechanism. *Yield of ethylene determined after leaving the resulting reaction mixture in an NMR tube at ambient temperature for another day. Ph, phenyl.

The proposed mechanism was further corroborated by density functional theory (DFT) calculations using Mo/**L1**/C_2H_4 and 2-[2-(1-methylcyclopropyl)phenyl]pyridine as a model metal complex and substrate, respectively (Fig. 4). Calculations with other possible conformations and model systems are provided in the Supporting Information. Gibbs free energies and enthalpies calculated at the UM06/SDD:6-31G(d,p) level of theory in mesitylene at 160 °C are shown here. The proximal selective cleavage of the C–C single bond proceeds from complex **A** with triplet ground state to afford molybdenacyclobutane **B** in its singlet state, during which spin crossover takes place. After this point, the singlet potential energy surface of the productive reaction path mostly lies lower than the triplet energy surface. The [2+2] cycloreversion from **B** affords molybdenum carbene **C** with coordinated ethylene. Dissociation of a pyridyl group from the molybdenum center (**C** to $\mathbf{D_{singlet}}$) and its intramolecular nucleophilic attack to the carbene affords the cyclized product ($\mathbf{D_{singlet}}$ to **E**).[43] The transition state Gibbs energies of each step relative to **A** were calculated to be 14.7, 5.9, and 14.3 kcal/mol, respectively.

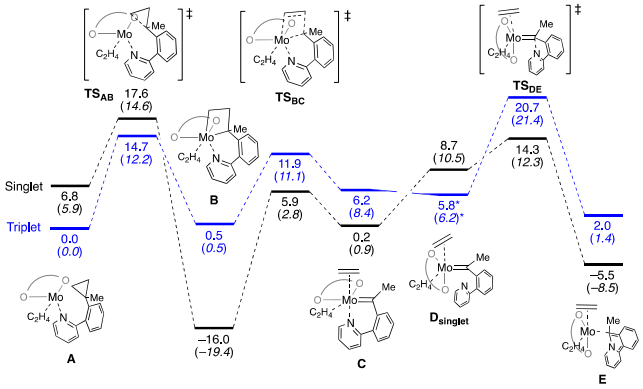

Figure 4. DFT-examined paths for the retro-cyclopropanation. Gibbs free energies and enthalpies (italicized) at 160 °C are given in kcal/mol, calculated at the UM06/SDD:6-31G(d,p)mesitylene(SMD) level of theory. *Ref. 43.

CONCLUSION

We have demonstrated that cyclopropanes can be used as uncommon C1 carbene units by releasing ethylene with a simple molybdenum/quinone catalyst. The strategic use of a pyridyl group with the catalyst enabled the efficient RC of cyclopropanes without extra strain, and the convenient synthesis of pyridoisoindole derivatives, compounds of interest for materials science. Although diazo compounds have played a leading role as sources of carbene species in organic synthesis, their inherent explosive and toxic nature continues to demand stable and safe surrogates for the generation of carbene species. The C1-fragment cyclopropane chemistry described here adds to the growing repertoire of non-diazo approaches to carbene species.[23] Investigations to expand the scope of cyclopropanes for the RC reactions by fine tuning of quinone ligands, are ongoing to further explore the applications of cyclopropanes as diazo surrogates.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures, DFT studies, physical properties of the compounds, and NMR spectra. 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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