ORGANIC CHEMISTRY
FRONTIERS

RESEARCH ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Org. Chem. Front.*, 2019, **6**, 1816

Rh(I)-Catalyzed intramolecular [3 + 2] cycloaddition reactions of yne-vinylidenecyclopropanes†

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Received 8th March 2019,
Accepted 2nd April 2019

DOI: 10.1039/c9qo00343f

rsc.li/frontiers-organic

A cationic Rh(I) complex-catalyzed intramolecular [3 + 2] cycloaddition reaction of newly developed yne-vinylidenecyclopropanes (VDCPs) has been established, affording an efficient synthesis of fused [6.5]-bicyclic structures in moderate to good yields under mild conditions. Moreover, the reaction exhibits a broad substrate scope along with good functional group tolerance.

Introduction

Bicyclic ring structures widely exist in natural products and are essential skeletons ubiquitously contained in some biologically important compounds possessing various biological activities.[1] Therefore, developing new methods to synthesize bicyclic scaffolds has been intensively pursued by the synthetic community. During the past few decades, rhodium-catalyzed C–C bond activation reactions and cycloadditions have emerged as one of the most powerful and straightforward methods in terms of good atom economy and mild reaction conditions for the construction of complex polycyclic frameworks.[2] Methylenecyclopropanes (MCPs),[3,4] vinylcyclopropanes (VCPs)[5,6] and vinylidenecyclopropanes (VDCPs)[7,8] as highly strained but readily accessible and adequately reactive molecules have been frequently used in the rapid construction of polycyclic skeletons since they are fascinating building blocks for organic synthesis. Recently, many interesting transformations have been explored using novel functionalized alkylidenecyclopropanes as substrates upon transition metal catalysis. These reactions can provide diversified polycyclic products with high chemo- and regioselectivities under mild conditions. Our research group has long been interested in discovering transition metal-catalyzed intramolecular cycloadditions of functionalized VDCPs for the construction of polycyclic frameworks. Previously, we reported an intramolecular [2 + 2] cycloaddition of yne-VDCPs **I-1** for the production of cyclopropane containing polycyclic compounds (Scheme 1a).[9] In this cycloaddition reaction, the coordination of the rhodium(I) complex to the internal double bond of the allene unit and the alkyne moiety formed intermediate **II-1**, which subsequently underwent cyclometalation/reductive elimination to afford the corresponding polycyclic products **IV-1**. In 2012, a highly efficient Rh(I)-catalyzed Pauson–Khand-type [2 + 2 + 1] cycloaddition of ene-VDCPs **I-2** with CO was achieved by our group (Scheme 1b).[10] The reaction proceeded through a cyclometalation of **I-2** with a Rh(I) catalyst to give rhodacyclic intermediate **II-2**, which underwent the insertion of CO to provide two regioisomers, **III-2** and **IV-2**. These reactive species underwent reductive elimination to afford the corresponding cyclopropane containing polycyclic adducts **V-2** in good yields. In this context, we report a cationic Rh(I) complex-catalyzed intramolecular [3 + 2] cycloaddition of newly developed yne-VDCPs **1** to afford a variety of bicyclic derivatives **2** with good functional group tolerance under mild conditions. On the basis of previous work, we envisaged that the cyclometalation of the Rh catalyst with the alkyne group and the double bond adjacent to the VDCP moiety could initially give intermediate **I-3**, which would directly undergo a β-carbon elimination to form the corresponding π-allyl Rh(III) intermediate **II-3**. The subsequent reductive elimination of intermediate **II-3** could give the desired bicyclic product **2** (Scheme 1c). In this intramolecular [3 + 2] cycloaddition reaction, the cyclopropane could act as a three-carbon synthon to give the corresponding ring-opened products rather than the cyclopropane ring retaining polycyclic products. It should be mentioned here that in 2014 we disclosed a gold(I)-catalyzed cycloisomerization of yne-VDCPs for the synthesis of bicyclic derivatives.[8j] However, these reactions underwent 5-*exo*-dig and 6-*exo*-dig cyclizations at the same time, giving bicyclic derivatives as well as VDCP-rearranged products as product mixtures in most cases since gold(I) catalysts are the most powerful soft Lewis acids for electrophilic activation of C–C triple bonds, rendering difficulties

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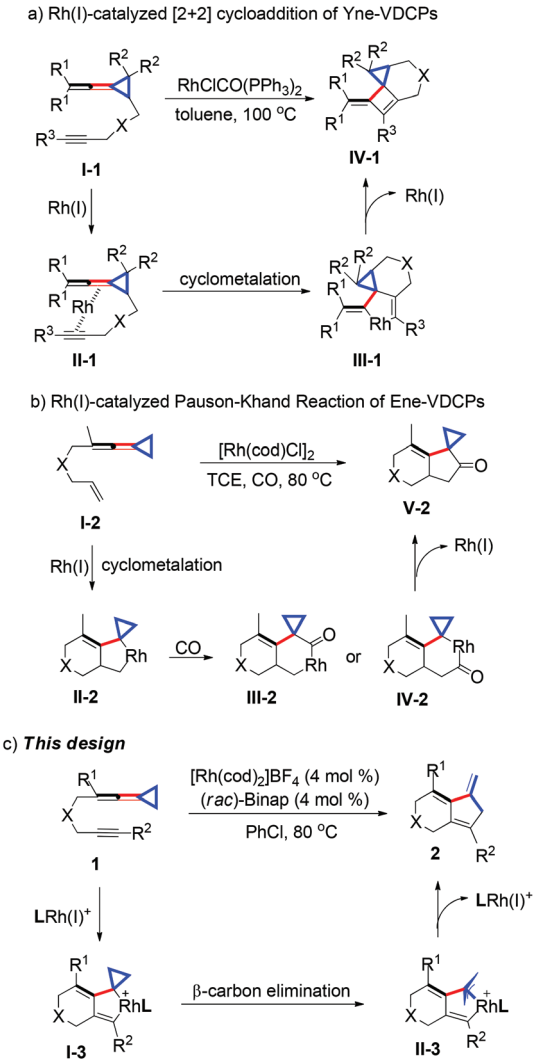
†Electronic supplementary information (ESI) available: Experimental procedures, characterization data of new compounds. See DOI: 10.1039/c9qo00343f



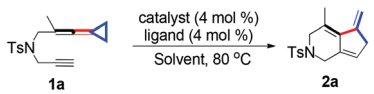
Scheme 1 Previous work and this work.

in the control of the regioselectivity. In addition, the gold-catalyzed reaction was limited to the use of terminal alkynes as substrates. On the other hand, rhodium(I) catalysts prefer to undergo oxidative addition in the reactions using ene-VDCPs or yne-VDCPs as substrates. Therefore, it is possible to overcome the shortage in the control of regioselectivity in the gold (I) catalyzed transformation and enable extension of the substrate scope and to afford bicyclic products exclusively if using a rhodium(I) complex as the catalyst.

Results and discussion

Our initial examination started with the tosylamide tethered yne-VDCP substrate **1a**. Thus, a solution of **1a** in 1,2-dichloroethane (DCE) was heated at 80 °C in the presence of 4 mol% of $[Rh(cod)_2]BF_4$ and 4 mol% of (*rac*)-Binap. To our delight, the desired bicyclic product **2a** was exclusively produced in 45% yield (Table 1, entry 1). With this encouraging result, we then

Table 1 Optimization of the reaction conditions



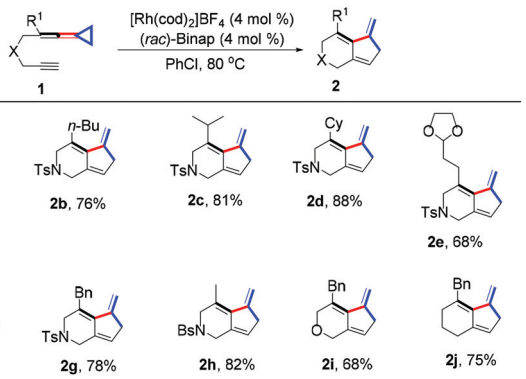
Entry[a]	Catalyst	Ligand	Solvent	Yield[b] [%]
1	$[Rh(cod)_2]BF_4$	(*rac*)-Binap	DCE	45
2	$[Rh(cod)_2]BF_4$	(*rac*)-Binap	Dioxane	62
3	$[Rh(cod)_2]BF_4$	(*rac*)-Binap	CH_3CN	21
4	***[Rh(cod)$_2$]BF$_4$***	***(rac)-Binap***	***PhCl***	***83***
5	$[Rh(cod)_2]BF_4$	^{t}BuXPhos	PhCl	48
6	$[Rh(cod)_2]BF_4$	dppe	PhCl	68
7	$[Rh(cod)_2]BF_4$	dppf	PhCl	61
8	$[Rh(cod)_2]BAr_F$	(*rac*)-Binap	PhCl	72
9[c]	$[Rh(cod)_2]BF_4$	(*rac*)-Binap	PhCl	78

[a] Reaction conditions: **1a** (0.1 mmol), catalyst (4 mol%), ligand (4 mol%), and solvent (2 mL) were used; 6–10 h. [b] Isolated yield. [c] The reaction was conducted at 90 °C.

focused our efforts on seeking out the optimal reaction conditions. Screening of solvents indicated that PhCl was the best choice, providing **2a** in 83% yield (Table 1, entries 1–4). A subsequent survey of other phosphine ligands revealed that using (*rac*)-Binap as the ligand gave **2a** in the highest yield (Table 1, entries 5–7). In addition, using $NaBAr_F$ as a coordinating anion afforded **2a** in 72% yield under otherwise identical conditions and raising the reaction temperature to 90 °C did not give a better result (Table 1, entries 8–9).

With the optimal reaction conditions in hand, we next examined the scope of the substrates and the results are shown in Table 2. For yne-VDCPs **1b–1e**, in which R^1 could be various primary or secondary alkyl groups, the desired products **2b–2e** were given in good yields ranging from 68–88%. The R^1 group could also be a 1-butenyl or benzyl group, giving the corresponding products **2f** and **2g** in 72% and 78% yields, respectively. Moreover, with the substrates **1h–1j**, in which the yne and VDCP moieties are connected by BsN, oxygen atom

Table 2 Substrate scope of the intramolecular cycloaddition of yne-VDCPs **1**[a,b]

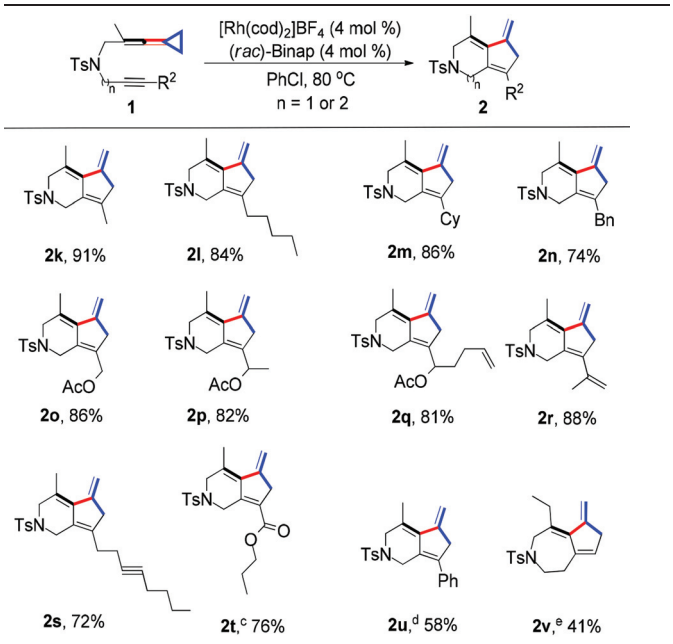


[a] Reaction conditions: yne-VDCP **1** (0.10 mmol), $[Rh(cod)_2]BF_4$ (4.0 mol%), (*rac*)-Binap (4.0 mol%), and PhCl (2.0 mL) were added and the reaction mixture was stirred for 6–8 h. [b] Isolated yield.

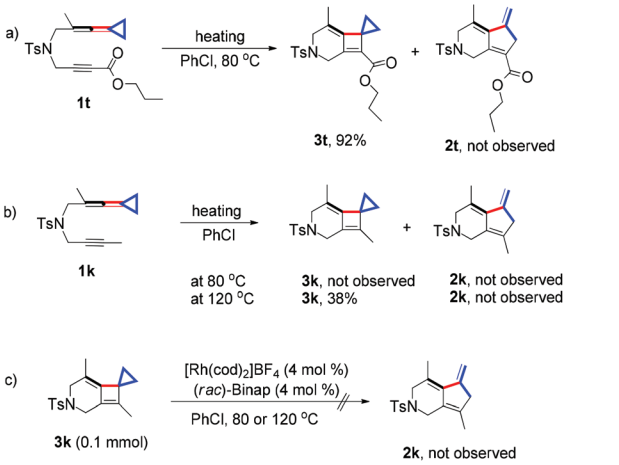
and carbon anchor, the corresponding products **2h–2j** were obtained in moderate to good yields as well.

Next, various substituents at the alkynyl moiety were explored (Table 3). When R^2 was a methyl, pentyl or cyclohexyl group, the desired products **2k–2m** were obtained in good to excellent yields. R^2 could also be a benzyl group, giving the corresponding product **2n** in 74% yield. For substrates **1o–1q**, in which the alkyne moiety contained a primary or secondary acetoxyalkyl group, the desired products **2o–2q** were produced in good yields ranging from 81–86%. In order to further explore the substrate scope of this protocol, substrates **1r** and **1s**, in which their alkynyl moieties have an olefinic group and an internal alkyne unit, were synthesized and the expected products **2r** and **2s** were produced in 88% and 72% yields respectively under the standard conditions. Previously, we also reported a thermal induced intramolecular [2 + 2] cycloaddition of alkynone-vinylidenecyclopropanes under heating conditions.[11a] Substrate **1t** bearing an α,β-unsaturated alkynyl ester was also tolerated, affording the desired product **2t** in 76% yield. Notably, in this case, substrate **1t** could be partially converted into a thermal-induced intramolecular [2 + 2] cycloaddition byproduct **3t** in 20% yield.[11] Moreover, using **1u** as the substrate, in which R^2 = Ph, the desired product **2u** was obtained in 58% yield along with its thermal-induced [2 + 2] cycloadduct **3u** as a product mixture. Extending the carbon chain with a $(CH_2)_2$ tether, the desired product **2v** could be exclusively obtained in 41% yield if using 1,2-dichloroethane (DCE) as the solvent. All these results indicated a broad substrate scope for this Rh(I)-catalyzed synthetic protocol.

Table 3 Substrate scope of the intramolecular cycloaddition of yne-VDCPs **1** [a,b]



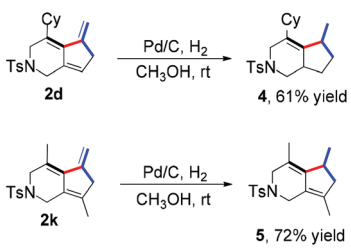
[a] Reaction conditions: yne-VDCP **1** (0.10 mmol), $[Rh(cod)_2]BF_4$ (4.0 mol%), (*rac*)-Binap (4.0 mol%), and PhCl (2.0 mL) were added and the reaction mixture was stirred for 6–8 h. [b] Isolated yield. [c] Byproduct **3t** was obtained in 20% yield (see Scheme 2). [d] Byproduct **3u** was obtained in 29% yield. [e] DCE was employed as the solvent in place of PhCl.



Scheme 2 Control experiments.

Control experiments were conducted to probe the mechanism of this cycloaddition reaction. In the case of **1t**, upon heating **1t** at 80 °C in PhCl for 12 h in the absence of the cationic Rh(I) catalyst, product **3t** could be obtained in 92% yield without formation of product **2t** (Scheme 2a). For substrate **1k**, although none of the [2 + 2] cycloadduct **3k** could be detected at 80 °C, 38% yield of **3k** could be afforded upon heating at 120 °C in PhCl for 48 h also without formation of **2k** (Scheme 2b). Furthermore, treating **3k** under the standard conditions did not give the corresponding [3 + 2] cycloadduct **2k** even if carrying out the reaction at 120 °C (Scheme 2c). This result suggested that the cyclobutene moiety could not undergo oxidative addition with the cationic Rh(I) complex, although the oxidative addition to cyclobutenones could take place smoothly.[12] Therefore, the initial oxidative addition of yne-VDCP **1** to give intermediate **I-3** is essential in this Rh(I)-catalyzed transformation (Scheme 1c).

Further transformations of the present product **2** were also examined briefly. The hydrogenation of **2d** and **2k** in methanol under H_2 atmosphere in the presence of Pd/C could give the corresponding products **4** and **5** in 61% and 72% yields, respectively (Scheme 3).



Scheme 3 The further transformation of products **2**.

Conclusions

In conclusion, we have developed a novel Rh(I)-catalyzed intramolecular [3 + 2] cycloaddition of yne-VDCP substrates, giving the corresponding fused [6.5]-bicyclic products in good yields under mild conditions. The substrate scope is broad along with good functional group tolerance allowing the easy generation of various carbo- and heterobicyclic compounds under mild conditions. This Rh(I)-catalyzed synthetic strategy significantly extended the substrate scope for the construction of bicyclic derivatives as compared with those of gold(I)-catalyzed cycloisomerizations.[8j] Additional efforts on the investigation of the mechanistic details of this intramolecular [3 + 2] cycloaddition reaction and application of this protocol to the synthesis of biologically active substances are currently ongoing in our laboratory.

Experimental section

General experimental methods

Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. NMR spectra were recorded with a Bruker spectrometer at 400 MHz (^{1}H NMR), and 100 MHz (^{13}C NMR) in $CDCl_3$, respectively. Chemical shifts were reported in ppm downfield from internal TMS. Organic solvents used were dried by standard methods when necessary. Commercially available reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure. Infrared spectra were recorded on a PerkinElmer PE-983 spectrometer with absorption in cm^{-1}. Mass spectra were recorded by ESI and HRMS was measured on an HP-5989 instrument.

General procedure for the synthesis of 2

A 10 mL dried tube was charged with yne-VDCP **1** (0.1 mmol, 1.0 equiv.), $[Rh(cod)_2]BF_4$ (4.0 mol%) and (*rac*)-Binap (4.0 mol%). The reaction tube was evacuated and backfilled with argon (repeated three times). Then, PhCl (2.0 mL) was added into the tube. The reaction mixture was stirred at 80 °C for 6–8 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO_2) to give the corresponding product **2**.

4-Methyl-5-methylene-7-pentyl-2-tosyl-2,3,5,6-tetrahydro-1*H*-cyclopenta[*c*]pyridine (2l). A light yellow oil, 84% yield (31 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.63 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 5.16 (s, 1H), 5.06 (s, 1H), 3.94 (s, 2H), 3.75 (s, 2H), 2.95 (s, 2H), 2.38 (s, 3H), 2.12 (t, J = 8.0 Hz, 2H), 1.82 (s, 3H), 1.22–1.41 (m, 6H), 0.89 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 145.0, 143.4, 137.5, 135.1, 134.0, 129.4, 129.2, 127.6, 119.9, 109.0, 50.2, 43.3, 41.5, 31.7, 28.3, 27.5, 22.5, 21.4, 17.4, 14.0; IR (CH_2Cl_2): ν 3022, 2938, 2813, 1659, 1547, 1402, 1282, 1174, 1058, 917, 947, 819, 759, 721, 630 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{30}NO_2S$ $(M + H)^+$ requires: 372.1992, Found: 372.1985.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

We are grateful for the financial support from the National Basic Research Program of China [(973)-2015CB856603], the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB20000000 and sioczz201808), the National Natural Science Foundation of China (20472096, 21372241, 21572052, 20672127, 21421091, 21372250, 21121062, 21302203, 21772037, 21772226, 20732008, 21772037, 21772226 and 21861132014), and the Fundamental Research Funds for the Central Universities 222201717003.

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