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Generation of Rhodium(I) Carbenes from Ynamides and Their Reactions with Alkynes and Alkenes

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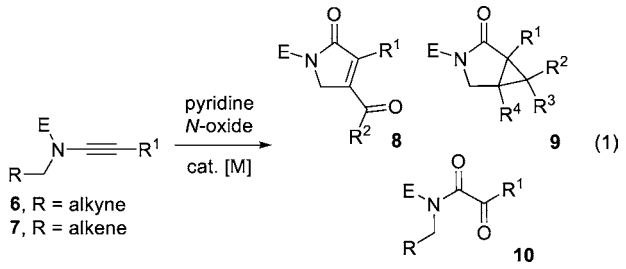
Supporting Information

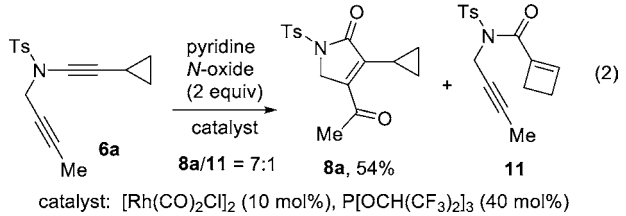
ABSTRACT: Rh(I) carbenes were conveniently generated from readily available ynamides. These metal carbene intermediates could undergo metathesis with electron-rich or neutral alkynes to afford 2-oxopyrrolidines or be trapped by tethered alkenes to yield 3-azabicyclo[3.1.0]-hexanes, a common skeleton in numerous bioactive pharmaceuticals. Although the scope of the former is limited, the latter reaction tolerates various substituted alkenes.

Metal carbenes are among the most important intermediates in organic synthesis and are involved in numerous reactions such as cyclopropanation, C−H insertion, dipolar cycloaddition, and metathesis reactions.[1] The most frequently used method for the preparation of metal carbenes is the decomposition of diazo compounds or related derivatives. In view of the hazardous and potential explosive nature of diazo compounds, other alternative carbene precursors are highly desirable. Recently, readily available ynamides[2,3] have emerged as versatile carbene precursors, and in particular, oxidation of ynamide **1** by dimethyl dioxirane (DMDO)[4] or other oxidants[5] was shown to afford the push−pull α-oxo carbene **3** through oxirene intermediate **2** (Scheme 1). Interestingly, a complementary α-oxo gold carbene, **5** (M = Au), was formed via intermediate **4** in the presence of gold catalysts and mild external oxidants (e.g., pyridine *N*-oxide).[6,7]

We envisioned that the choice of metal catalyst and ligand would have a significant impact on the reactivity of carbene **5**. We herein report that α-oxo Rh(I) carbenes **5** (M = Rh) can be generated from ynamides **6** and **7** and then react with the tethered alkyne or alkene to afford heterocycles **8** and **9**, respectively (eq 1). In contrast, keto imide **10** was often the predominant product observed by us and others in the presence of gold(I) catalysts.[6]



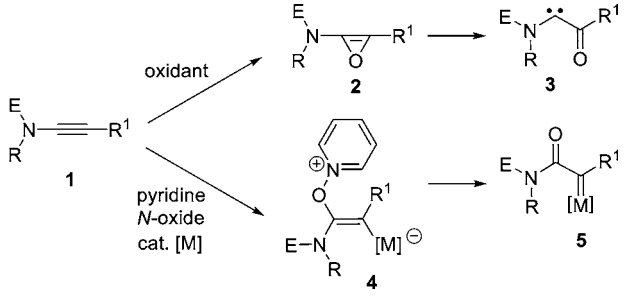
Our interest in the chemistry of cyclopropyl metal carbenes[8] and π-acidic Rh(I) complexes[9] prompted us to investigate the possibility of generating Rh(I) carbenes[10] from ynamide **6a** for cycloisomerization reactions. We prepared ynamide **6a** and then treated it with pyridine *N*-oxide and a complex formed from $[Rh(CO)_2Cl]_2$ and $P[OCH(CF_3)_2]_3$ (eq 2); this complex



was shown to be successful in promoting acyloxy migration of propargylic esters,[11] a process that is typically catalyzed by π-acidic transition metals.[9,12] Compound **8a** was isolated as the major product, and cyclobutene **11** was also observed as the minor product. A metal carbene similar to intermediate **5** was presumably generated from ynamide **6a** through the mechanism shown in Scheme 1. Ring expansion of this metal carbene intermediate would produce cyclobutene **11**.[8]

When the cyclopropyl group was replaced by other substituents, the formation of cyclobutene was avoided, and a

Scheme 1. Complementary Carbenes from Ynamides



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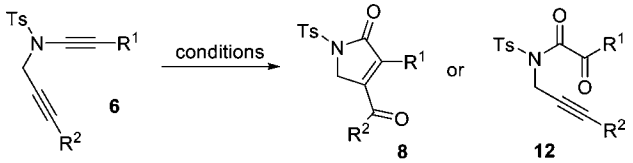
62% yield of cycloisomerization product **8b** was obtained from diyne **6b** under the conditions employed for diyne **6a** (Table 1, entry 1). The structure of product **8b** was unambiguously assigned by X-ray analysis.[13] The oxidative cycloisomerization of diyne **6b** was then optimized under different conditions. Keto imide **12b** appeared when the phosphite ligand was removed (entry 2).[14] Other ligands produced worse results (entries 3 and 4). No reaction occurred when $Rh_2(OAc)_4$ was used as the catalyst (entry 5). Interestingly, only keto imide **12b** was observed when a gold catalyst was employed (entry 6). Using $PtCl_2$ as the catalyst provided a complex mixture (entry 7). We then examined different substituted pyridine *N*-oxides, such as *p*-methoxy-, *p*-nitro-, 2,6-dichloro-, and 3,5-dichloropyridine *N*-oxide. Among them, 3,5-dichloropyridine *N*-oxide provided the best result (entry 8). Among all of the solvents that we screened, dioxane afforded the highest yield (entry 9). No desired product was obtained when other rhodium complexes, such as $[Rh(COD)Cl]_2$ (COD = 1,5-cyclooctadiene), Wilkinson's catalyst, and $[Rh(COD)BF_4]$ were employed.

Table 1. Screening of Conditions for the Oxidative Cycloisomerization of Diyne 6[a]



6b, **8b**, and **12b**: R^1 = Ph, R^2 = *p*-$MeOC_6H_4$

Entry	Conditions	8b:12b[b]	Yield[c]
1	$[Rh(CO)_2Cl]_2$ (5 mol %), $P[OCH(CF_3)_2]_3$ (20 mol %)	1:0	62%
2	$[Rh(CO)_2Cl]_2$ (5 mol %)	5:1	–
3	$[Rh(CO)_2Cl]_2$ (5 mol %), $P(OPh)_3$ (20 mol %)	no reaction	
4	$[Rh(CO)_2Cl]_2$ (5 mol %), $[3,5\text{-}(CF_3)_2C_6H_3]_3P$ (20 mol %)	5:1	–
5	$Rh_2(OAc)_4$ (5 mol %)	no reaction	
6	$Au(PPh_3)Cl$ (10 mol %), AgOTf (10 mol %)	0:1	–
7	$PtCl_2$ (5 mol %)	complex mixture	
8[d]	see entry 1 for catalyst	1:0	70%
9[d,e]	see entry 1 for catalyst	1:0	78%

[a]Conditions: pyridine *N*-oxide (3 equiv), $ClCH_2CH_2Cl$, 80 °C, 4 h, unless noted otherwise. [b]Determined by ^1H NMR analysis of the crude product. [c]Isolated yields of **8b**. [d]3,5-Dichloropyridine *N*-oxide (3 equiv) was used as the oxidant. [e]Dioxane was used as the solvent.

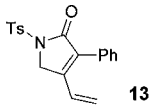
With the optimized conditions in hand, we investigated the scope of the oxidative cycloisomerization of diyne **6** (Table 2). The yield of product **8c** (R^2 = Ph) was slightly lower than that of **8b**. The reaction tolerated substrates with an ortho-substituted aryl group as R^2 or R^1 (substrates **6d** and **6e**, respectively). When R^2 was an electron-deficient aryl group (e.g., *p*-ClC_6H_4, *p*-$NO_2C_6H_4$), a complex mixture was obtained. For R^2 = Me (substrate **6f**), diene **13** was isolated in 10% yield. For R^1 = H (substrate **6g**), the carbene became more reactive, and the reaction could be carried out even at room temperature. When R^1 was an alkyl group (substrate **6h**), 1,2-hydrogen migration product **14** was observed. For substrates **6i** and **6j** with a more functionalized R^1 or R^2 substituent, complex mixtures were observed.

We then examined the reactivity of α-oxo Rh(I) carbenes toward alkenes (Table 3, first entry). Under the previously optimized conditions for oxidative cycloisomerization of diynes, cyclopropanation product **9a** was obtained in 78% yield from enyne **7a**. No improvement was observed when different Rh(I) complexes, ligands, or other substituted pyridine *N*-oxides were screened. When $Au(PPh_3)Cl$/AgOTf was employed as the catalyst, keto imide **15a** was isolated as the major product together with small amount of cyclopropane **9a**. No reaction occurred when $Rh_2(OAc)_4$ was used as the catalyst.

Table 2. Oxidative Cycloisomerization of Diynes[a]

Substrate **6**	Product	Yield[b]
6c, R^1 = Ph, R^2 = Ph	**8c**	67%
6d, R^1 = Ph, R^2 = *o*-$MeOC_6H_4$	**8d**	76%
6e, R^1 = *o*-FC_6H_4, R^2 = *p*-$MeOC_6H_4$	**8e**	75%
6f, R^1 = Ph, R^2 = Me	**8f** + **13**	56% (10%)[c]
6g,[d] R^1 = H, R^2 = *p*-$MeOC_6H_4$	**8g**	80%
6h, R^1 = $PhCH_2CH_2CH_2$, R^2 = *p*-$MeOC_6H_4$	**8h** + **14**	67% (11%)[e]
6i, R^1 = H, R^2 = $CH_2OCH_2CH{=}CH_2$	complex mixture	
6j, R^1 = $CH{=}CHCH_2OCH_2CH{=}CH_2$, R^2 = *p*-$MeOC_6H_4$	complex mixture	

byproducts:



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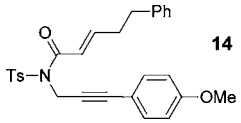

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[a]Conditions: $[Rh(CO)_2Cl]_2$ (5 mol %), $P[OCH(CF_3)_2]_3$ (20 mol %), 3,5-dichloropyridine *N*-oxide (3 equiv), dioxane, 80 °C, 4 h. [b]Isolated yields. [c]Yield of byproduct **13**. [d]Room temperature, 3 h. [e]Yield of byproduct **14**.

The scope of oxidative cycloisomerization of enyne **7** was then investigated (Table 3). For terminal ynamides **7b–e**, the reaction could be conducted at room temperature. Among these, terminal alkene **7b** produced the best yield. A 70% yield was obtained for cyclopropanation of nonsubstituted styrene **7c**. For diyne **6**, R^2 must be an electron-neutral or -rich aryl group to allow the oxidative cycloisomerization to proceed. On the other hand, it has been shown that the α-oxo Rh(I) carbene derived from 1,2-acyloxy migration of propargylic esters reacts only with electron-deficient alkynes or alkenes.[15] To our delight, both electron-rich and electron-poor styrenes underwent cyclopropanation, forming bicyclic products **9d** and **9e**, respectively. It is worth pointing out that a nitro group, which has been used as external oxidant in gold catalysis,[7r] can be tolerated.

Alkene and ether functionalities in the R^1 substituent can be tolerated (substrate **7f**). Surprisingly, when R^1 was an alkyl group (substrate **7g**), hydrolysis product **16** was obtained. A complex mixture was observed when an olefin functional group was introduced in the R^2 substituent (substrate **7h**). Alkenes with *gem*-dimethyl substitution (**7i**) or a methyl group at the internal position (**7j**) participated in the cyclopropanation, yielding products **9i** and **9j**, respectively. A six-atom tether was also tolerated, affordinig bicyclic product **9k** in 78% yield.

It is generally easier to remove a nosyl group than a tosyl group.[16] We were pleased to find that the yields of products **9l** and **9m** were comparable to those of their tosyl counterparts **9a** and **9b**. The nosyl group in product **9o** was removed

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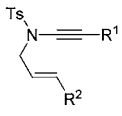
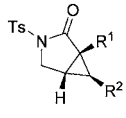
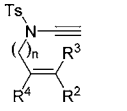
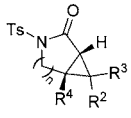
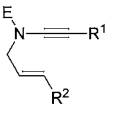
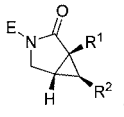
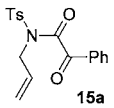
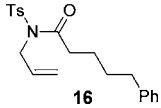
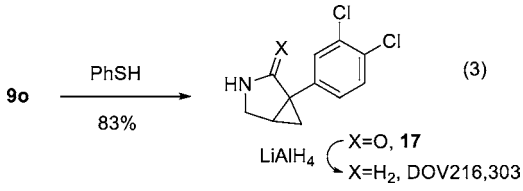
Table 3. Oxidative Cycloisomerization of Enynes[a]

Substrate **7**	Product	Yield[b]
 (**7a** – **7h**)	 (**9a** – **9h**)	
7a,[c] R^1 = Ph, R^2 = H	**9a**	78%
7b, R^1 = H, R^2 = H	**9b**	88%
7c, R^1 = H, R^2 = Ph	**9c**	70%
7d, R^1 = H, R^2 = *p*-$MeOC_6H_4$	**9d**	62%
7e, R^1 = H, R^2 = *p*-$NO_2C_6H_4$	**9e**	63%
7f,[c] R^1 = $CH{=}CHCH_2OBn$, R^2 = H	**9f**	78%
7g,[c] R^1 = $(CH_2)_3Ph$, R^2 = H	**16**	68%
7h, R^1 = H, R^2 = $CH_2OCH_2CH{=}CH_2$	complex mixture	
 (**7i** - **7k**)	 (**9i** - **9k**)	
7i, R^2 = R^3 = CH_3, R^4 = H, n=1	**9i**	87%
7j, R^2 = R^3 = H, R^4 = CH_3, n=1	**9j**	72%
7k, R^2 = R^3 = R^4 = H, n=2	**9k**	78%
 (**7l** – **7o**)	 (**9l** – **9o**)	
7l, E = *p*-Ns, R^1 = H, R^2 = H	**9l**	80%
7m[c] E = *p*-Ns, R^1 = Ph, R^2 = H	**9m**	76%
7n,[c] E = *p*-Ns, R^1 = *p*-$CH_3C_6H_4$, R^2 = H	**9n**	60%
7o,[c] E = *o*-Ns, R^1 = 3,4-$Cl_2C_6H_3$, R^2 = H	**9o**	81%
byproducts:  **15a**	 **16**	

[a]Conditions: $[Rh(CO)_2Cl]_2$ (5 mol %), $P[OCH(CF_3)_2]_3$ (20 mol %), 3,5-dichloropyridine *N*-oxide (1.0 equiv), dioxane, room temperature, 2 h. [b]Isolated yields. [c]80 °C, 4–8 h.

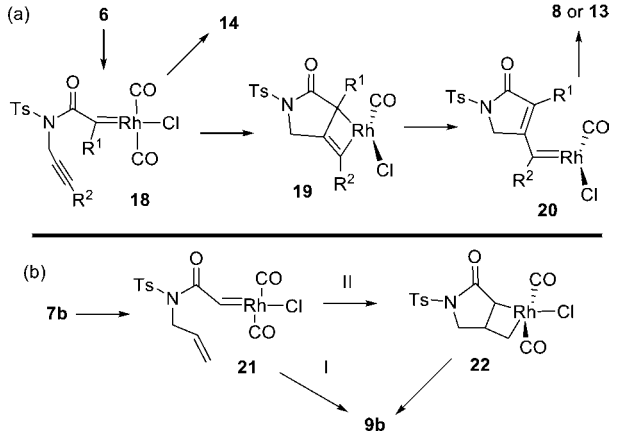
smoothly under mild conditions to yield compound **17** (eq 3),[16] which is the precursor for the triple-reuptake inhibitor



DOV216,303.[17,18] The 3-azabicyclo[3.1.0]hexane skeleton[19] is also present in numerous other pharmaceuticals with broad biological activities, such as analgesics, antibacterials, and aromatase inhibitors.[17,20]

The proposed mechanisms for the oxidative cycloisomerizations of diynes and enynes are shown in Scheme 2. Metal carbenes **18** and **21** can be generated from ynamides **6** and **7b**, respectively, following the mechanism shown in Scheme 1. Metathesis of metal carbene **18** with the tethered alkyne

Scheme 2. Proposed Mechanisms for Oxidative Cycloisomerizations of (a) Diynes and (b) Enynes



through metallacyclobutene **19** may afford a new carbene, **20**,[21] which can be oxidized by pyridine *N*-oxide to yield product **8**. When R^1 or R^2 was an alkyl group, 1,2-hydrogen migration produced small amount of byproduct **14** or **13**, respectively. Density functional theory (DFT) calculations indicated that the barrier for the conversion of **18** to **20** is 20.7 kcal/mol and that this process can take place at room temperature.[13] Rh(I) carbene **21** may react with the tethered alkene to form product **9b** via two pathways: (I) a concerted cyclopropanation and (II) metathesis followed by reductive elimination through intermediate **22**. DFT calculations suggested that pathway I is preferred because the reductive elimination from intermediate **22** in pathway II is relatively difficult.[13]

In summary, we have developed an efficient method for the generation of *α*-oxo Rh(I) carbenes from ynamides.[10] We have demonstrated that the $[Rh(CO)_2Cl]_2/P[OCH(CF_3)_2]_3$ complex is acidic enough to mediate the addition of an external oxidant to ynamides under mild conditions. The Rh(I) carbenes produced from this process can then react with electron-rich or neutral alkynes or various substituted alkenes to afford 2-oxopyrrolidines and 3-azabicyclo[3.1.0]hexanes, respectively. Further studies of the novel reactivity of Rh(I) carbenes are underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, characterization data, and spectra (IR, ^1H and ^{13}C NMR, and HRMS). 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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