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Synthesis of Trisubstituted Pyrroles from Rhodium-Catalyzed Alkyne Head-to-Tail Dimerization and Subsequent Gold-Catalyzed Cyclization

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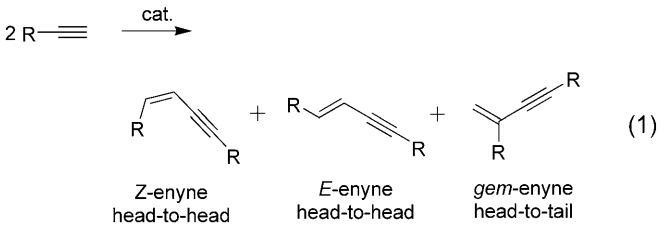
Abstract: Dimerization of *N*-protected propargylic amines in a rather rare head-to-tail mode has been achieved under mild conditions with high selectivity using rhodium catalysts. The *N*-protecting group could be a sulfonyl, carbamate, or carbonyl functionality and (cyclooctadiene)rhodium chloride dimer/1,1′-bis(diphenylphosphino)ferrocene {[Rh(COD)Cl]$_2$/dppf} as well as tris(triphenylphosphine)rhodium chloride [Rh(PPh$_3$)$_3$Cl] proved to be active catalysts. In addition, these functionalized *gem*-enynes subsequently undergo selective gold(III)-catalyzed intramolecular hydroamination to give trisubstituted pyrroles under mild conditions.

Keywords: enynes; gold; head-to-tail dimerization; hydroamination; propargylic amines

Introduction

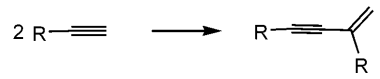
It remains a challenge to develop catalytic systems that efficiently promote the selective formation of carbon-carbon bonds by combining several simple molecules.[1] 1-Alkyne dimerization reactions are attractive in that enynes are atom-economically produced which are important building blocks in organic synthesis.[2] Three isomeric products, *Z*-, *E*-, and *gem*-enynes can be possible as a result of the regio- and stereoselectivity [Eq. (1)]. While it has been realized that the identity of phosphine ligands and the steric bulk of alkyne substrates play important roles in the regio- and stereoselectivity of alkyne dimerization reactions catalyzed by phosphine complexes,[3] controlling the selectivity to favor *Z*- and *gem*-enyne products remains a task. In general, late transition metal-catalyzed alkyne dimerization reactions tend to give *E*-enynes,[4–7] while organolanthanide catalysts often give the corresponding *Z*-enyne products.[8] For instance, the yields of *Z*-enynes can even be as high as 99% using lutetium half-metallocene catalysts, and mechanistic studies have shown that dimeric lutetium intermediates are responsible for this selectivity.[8a] In addition, ruthenium catalysts have also been reported for selective *Z*-dimerization.[9]



(1)

In sharp contrast, examples of selective head-to-tail dimerization of alkynes are rather rare although reports in this context span over two decades.[10] In most cases the substrates are limited to simply alkyl- or arylalkynes (Table 1). Trost and co-workers reported one of the few examples of efficient dimerization of heteroatom-functionalized alkynes in this mode.[10b] In view of the poor or under-explored functional group compatibility in alkyne dimerization in this mode, we now report a successful case of dimerization of *N*-protected propargylamines. Moreover, these *gem*-enyne

Table 1. Examples of selective alkyne dimerization in a head-to-tail mode.



Catalyst	R	Yield [%]	Ref.
$[Ru(dppm)_2(\mu\text{-}CH_2)(CO)_2]_2$	Ph or *n*-Bu	not reported	[9e]
$[(Et_2N)_3U]BPh_4$	*i*-Pr	75	[9d]
MAO	*n*-Bu, *i*-Pr, or Ph	>99	[9c]
$[Rh(PMe)_3Cl]_2$	Ph	>99	[9a]
$Pd(OAc)_2/P[2,4\text{-}C_4H_3(OMe)_2]_3$	Ph or *n*-hexyl	62–63	[9b]

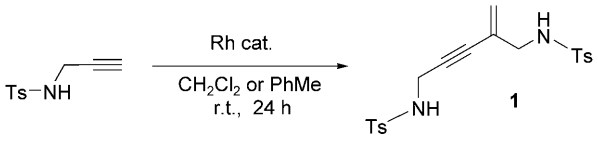
products can subsequently undergo Au-catalyzed intramolecular hydroamination reactions to afford important 2-(aminomethyl)pyrrole derivatives which have been used in molecular recognition[11a,b] and in the pharmaceutical industry as pharmacologically active compounds or central nervous system depressants.[11c,d] Moreover, pyrroles are important building blocks in organic synthesis[12] and are widely used for biological studies.[13]

Results and Discussion

The dimerization of propargylamines is an important reaction in that the functionalized enyne products could allow further intramolecular elaboration. However, no selective head-to-tail dimerization has been reported for such substates. Recent studies by Miura and co-workers seem to suggest that simple propargylamines or alcohols have poor reactivity toward homodimerization when catalyzed by rhodium complexes.[4b] We reason that $TsNHCH_2C{\equiv}CH$ might show superior selectivity and reactivity in that the tosyl oxygen is potentially a weak donor,[14] and the introduction of a withdrawing Ts group should tune the electronic effects of the C≡C bond. We also noted that simple rhodium complexes such as $Rh(PPh_3)_3Cl$[15] and $[Rh(COD)Cl]_2$/phosphines[4b] have been applied as catalysts for the head-to-tail dimerization of alkynes. We hope that the introduction of a Ts group could switch the selectivity to the rare head-to-tail mode even when using such simple rhodium complexes.

Indeed, the desired *gem*-enyne product (**1**) was obtained in 52% yield (toluene, 24 h, room temperature) when catalyzed by a combination of $[Rh(COD)Cl]_2$ (2 mol%) and PPh_3 (4 mol%), although 42% of the starting material remained intact (entry 1, Table 2). The NMR yield was improved to 64% when CH_2Cl_2 is used as the solvent (entry 2, Table 2), but essentially no further increase of the reaction yield could be achieved in CH_2Cl_2 under reflux. To our surprise,

Table 2. Optimization of reaction conditions.[a]



Entry	Catalyst	Solvent	NMR yield[b] [%]	SM[b] [%]
1	$[Rh(COD)Cl]_2/PPh_3$	PhMe	52	42
2	$[Rh(COD)Cl]_2/PPh_3$	CH_2Cl_2	64	31
3	$Rh(PPh_3)_3Cl$	CH_2Cl_2	83 (77[c])	10
4	$[Rh(COD)Cl]_2$/dppb	CH_2Cl_2	64	30
5	$[Rh(COD)Cl]_2$/dppf	CH_2Cl_2	90 (83[c])	5
6	$[Rh(COD)Cl]_2$/dppp	CH_2Cl_2	54	23
7	$[Rh(COD)Cl]_2$/dppm	CH_2Cl_2	<3	75
8	$[Rh(COD)Cl]_2$/xantphos	CH_2Cl_2	<3	95

[a] The reaction was carried out at 23 °C for 24 h under argon, using $TsNHCH_2C{\equiv}CH$ (0.25 mmol), $Rh(PPh_3)_3Cl$ (0.005 mmol) or $[Rh(COD)Cl]_2$ (0.005 mmol)/phosphine (0.01 mmol), 1,3,5-trimethoxybenzene (internal standard, 0.083 mmol), and CH_2Cl_2 (1.5 mL).

[b] Yields and starting material percentage were determined using 1.3.5-trimethoxybenzene as an internal standard by ^1H NMR spectroscopy.

[c] Isolated yield.

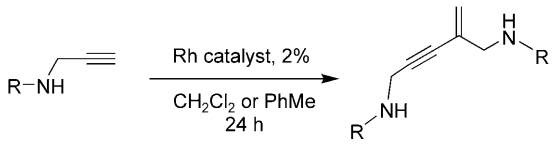
nearly no desired product was obtained when PPh_3 was replaced by PCy_3, P(*p*-$OMeC_6H_4)_3$ or P(*p*-$C_6H_4F)_3$ (entries 3 and 4, Table 2). $Rh(PPh_3)_3Cl$ was then applied as a catalyst, which has been reported to catalyze the dimerization of silyl-substituted acetylene to the corresponding (*E*)-enynes,[15] and the isolated yield of **1** was improved to 77% (entry 3, Table 2). It has been reported that bidentate phosphines have significant effects on the selectivity of alkyne dimerization,[4b,c] therefore, we screened dppb, dppf, dppp, dppm, and xantphos together with $[Rh(COD)Cl]_2$ in a 2:1 ratio,[16] among which dppf gave the best result (entries 5–8, Table 2). Thus, the isolated yield was further improved to 83% when $[Rh(COD)Cl]_2$/dppf was used as a catalyst (entry 5, Table 2).

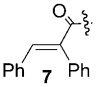
We thus retained $Rh(PPh_3)_3Cl$ and $[Rh(COD)Cl]_2$/dppf to further explore the scope of this reaction, and the results are given in Table 3. Various *N*-propargylcarbamates and ureas smoothly undergo dimerization under the same conditions. Moderate to good yields were obtained in the dimerization of $BocNHCH_2C{\equiv}CH$ (62%) and $CbzNHCH_2C{\equiv}CH$ (74%) when catalyzed by $Rh(PPh_3)_3Cl$ or $[Rh(COD)Cl]_2$/dppf (entries 3 and 4, Table 3). The $Rh(COD)Cl]_2$/dppf system shows an activity superior to that of $Rh(PPh_3)_3Cl$ in the dimerization of $Me_2NC(O)NHCH_2C{\equiv}CH$ (67%) or $EtOC(O)NHCH_2C{\equiv}CH$ (66%) (entries 5 and 6, Table 3). Dimerization of structurally related *N*-propargylamides is also achievable. However, in comparison with propargylcarbamates or ureas, amides with R = aryl or vinyl groups all showed lower activity and moderate to low yields (46–64%) were obtained in toluene even at 80 °C using $Rh(PPh_3)_3Cl$ as a catalyst (entries 7 and 8, Table 3). Interestingly, an amide with R = *tert*-butyl can dimerize with 78% isolated yield using the $[Rh(COD)Cl]_2$/dppf catalyst at room temperature (entry 9, Table 3). Although no detailed mechanism has been elucidated, it is possible that the *tert*-butyl group renders the amide group a stronger donor such that head-to-tail dimerization is facilitated.

In addition, both catalysts showed poor activity and selectivity for the dimerization of phenylacetylene, ethyl propiolate, and trimethylsilylacetylene under the same conditions. *N*-Sulfonylated propargylamines seem to be the most efficient substrates in this head-to-tail dimerization. We thus extend the substrates to such substrates with different sulfonamide functionalities. As shown in Table 4, all these substrates dimerize with moderate to high yields (67% to 83%).

Importantly, in all these *gem*-enyne products the proper orientation of the NH group and the neighboring C≡C bond allows further elaboration. Au,[17] Pd,[18] and Ir[19] complexes are known to activate alkenes and alkynes to allow catalytic hydroamination. In addition, examples have been reported for the cyclization of enynes to give furans[20], thiophenes[21], and pyrroles[22]. We initially attempted the hydroamination (*5-endo-dig* cyclization) of enyne **1** using $AuCl_3$ as a catalyst at room temperature. Although ^1H NMR analysis of the reaction mixture obtained showed no starting material after 1 h, the reaction suffered from poor selectivity in that product **18** was isolated in only 40% yield (entry 1, Table 5). The selectivity was dramatically improved by lowering the reaction temperature to −20 °C and the isolated yield was augmented

Table 3. Head-to-tail dimerization of functionalized 1-alkynes.[a]



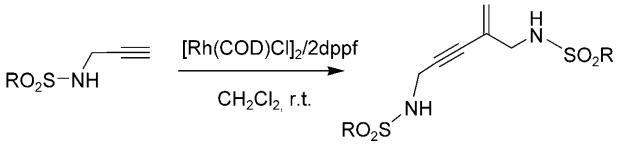
Entry	R	Catalyst (2 mol%)	Solvent	Temperature [°C]	Isolated yield [%]	Product
1	Ts	$[Rh(COD)Cl]_2$/2 dppf	CH_2Cl_2	24	83	**1**
2	Ts	$Rh(PPh_3)_3Cl$	CH_2Cl_2	24	77	**1**
3	Boc[b]	$[Rh(COD)Cl]_2$/2 dppf	CH_2Cl_2	24	62	**2**
4	Cbz[c]	$Rh(PPh_3)_3Cl$	CH_2Cl_2	24	74	**3**
5	$Me_2NC(O)$-	$[Rh(COD)Cl]_2$/2 dppf	CH_2Cl_2	24	67	**4**
6	EtOC(O)-	$[Rh(COD)Cl]_2$/2 dppf	CH_2Cl_2	24	66	**5**
7	PhC(O)-	$Rh(PPh_3)_3Cl$	PhMe	80	46	**6**
8		$Rh(PPh_3)_3Cl$	PhMe	80	64	**8**
9	*t*-BuC(O)-	$[Rh(COD)Cl]_2$/2 dppf	CH_2Cl_2	24	78	**9**

[a] *Reaction conditions:* alkyne substate (0.5 mmol), $[Rh(COD)Cl]_2$ (0.01 mmol)/dppf (0.02 mmol) or $Rh(PPh_3)_3Cl$ (0.01 mmol), CH_2Cl_2 or PhMe (1.5 mL), 24 h.

[b] Boc = *tert*-butyloxycarbonyl.

[c] Cbz = carbobenzoxy.

Table 4. Head-to-tail dimerization of propargyl sulfonamides.[a]



Entry	R	Time [h]	Isolated yield [%]	Product
1	Me	24	67	**10**
2	MeO–C6H4–	16	79	**11**
3	Br–C6H4–	16	80	**12**
4	$PhCH_2$	24	64	**13**
5	Cl–C6H4–	24	81	**14**
6	Me–C6H4–	16	83	**15**
7	Ph	15	79	**16**
8	*n*-Bu	24	72	**17**

[a] *Reaction conditions:* *N*-propargylamide (0.5 mmol), $[Rh(COD)Cl]_2$ (0.01 mmol), dppf (0.02 mmol), CH_2Cl_2 (1.5 mL), rt, 16-24 h.

to 88% after 0.7 h (entry 2, Table 5). The scope of the enyne substrates was extended to those with alkyl- or arylsulfonamide functionalities. Under differently optimized conditions (entries 3–10, Table 5), the isolated yields range from 70% to 88%. We noted that gold-catalyzed intramolecular hydroamination reactions have been reported to give substituted pyrroles.[23]

Cyclization of cabamate- or amide-functionalized enynes is also applicable, and the results are given in Table 5. Here the R group has pronounced effects on the cyclization process. Pyrrole **27** was isolated in 80% yield from the Cbz-substitited enyne **3** (−40 °C, 1 h) (entry 11, Table 5), while Boc-substituted pyrrole **28** was obtained in 50% yield (−40 °C, 2 h) (entry 12, Table 5). In line with the low yield of the dimerization step (Table 3), cyclization of **8** gave pyrrole product **30** in only 36% yield after initial optimerization (entry 14, Table 5). In sharp contrast, cyclization of compound **9** (with R = *t*-Bu) gave two isomeric oxazoles (*Z*)-**31** and (*E*)-**31** [Eq. (2)], instead of any pyrrole (see Supporting Information). The yield and the identity of the cyclization product seem to correlate with the acidity of the NH proton (entries 11–14, Table 5): a lower yield of pyrrole was obtained for an amide-substituted enyne (less acidic). In the cycliza-

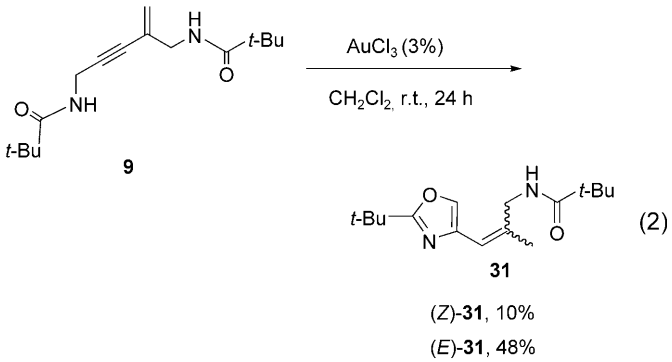
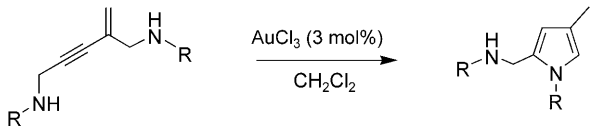


Table 5. Au-catalyzed cyclization of *N*-functionalized enynes.[a]



Entry	R	Temperature [°C]	Time [h]	Yield [%]	Product
1	Ts (**1**)	25	1	40	**18**
2	Ts (**1**)	−20	0.7	88	**18**
3	$MeSO_2$ (**10**)	25	1	75	**19**
4	*n*-$BuSO_2$ (**17**)	25	1	76	**20**
5	*p*-Br(C_6H_4)SO_2 (**12**)	0	2	81	**21**
6	$PhSO_2$ (**16**)	0	2	88	**22**
7	*p*-Cl(C_6H_4)SO_2 (**14**)	0	3	80	**23**
8	*p*-MeO(C_6H_4)SO_2 (**11**)	−20	3	83	**24**
9	*m*-Me(C_6H_4)SO_2 (**11**)	25	1	76	**25**
10	$PhCH_2SO_2$ (**13**)	0	2	70	**26**
11	Cbz (**3**)	−40	1	80	**27**
12	Boc (**2**)	−40	2	50	**28**
13	EtOC(O)- (**5**)	−40	2	52	**29**
14	PhC(O)- (**8**)	25	20	36	**30**

[a] *Reaction conditions:* enyne (0.5 mmol), $AuCl_3$ (3 mol%), and CH_2Cl_2 (2 mL).

tion of enyne **9**, only O-attack took place as a result of the low acidity of the NH group. Several examples of metal-mediated carbonyl attack on *terminal* alkynes have been recently reported.[24] A plausible mechanism of the overall transformation is proposed in Scheme 1. The C≡C bond in **9** is activated by $AuCl_3$ towards carbonyl attack (*5-exo-dig* cyclization) to give a gold vinyl intermediate, protonation of which affords an *exo*-cyclic olefin intermediate. The final product is proposed from the isomerization of this olefin intermediate to the more stable aromatic oxazole products.

Conclusions

Rare head-to-tail dimerization reactions of *N*-protected propargylic amines were achieved with moderate to high yields under mild conditions. Both $Rh(PPh_3)_3Cl$ and $[Rh(COD)Cl]_2$/dppf showed high catalytic activity with 2 mol% loading. The dimerization works most efficiently for enynes with a sulfonamide functionality, although still moderate to good yields could be obtained for the dimerization of enynes tethered to amide, carbamate, and urea functionalities. The enyne products can further undergo Au-catalyzed hydroamination to afford trisubstituted pyrroles. For the hydroamination of amide-functionalized enynes, either oxygen or nitrogen can attack the neighboring triple bond, depending on the substituents attached to the carbonyl group. Studies of factors that favor this dimerization mode, the scope of cross-dimerization and homodimerization of other substrates in this mode, and product functionalization other than hydroamination are currently in progress in our laboratory.

Experimental Section

General Remarks

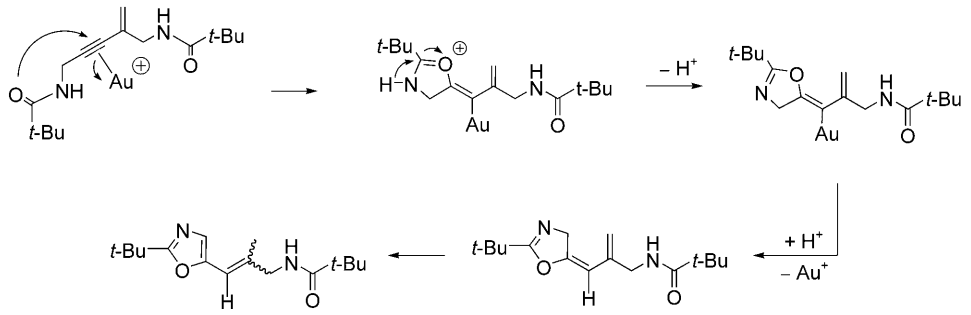
All commercial solvents were dried using 4 Å molecular sieves, and all commercial reagents were used as received. Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plates (0.2 mm thickness). TLC plates were visualized using UV radiation (254 nm) or by staining with a basic solution of $KMnO_4$. IR spectra were recorded on a Horiba FT 300-S by the ATR method and on a Shimazu IR Prestige-21 FT-IR spectrometer. High-resolution mass spectra were obtained with a Finnigan MAT 95 XP mass spectrometer (EI) and a Waters Micromass Q-Tof Premier mmass spectrometer (ESI). Melting points were recorded on an SRS MPA100 automated melting point system. Microanalyses were performed by the Elemental Analysis Laboratory of the Division of Chemistry and Biological Chemistry, Nanyang Technological University. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX 300, Bruker AMX 400, or Bruker DRX 500 spectrophotometer. Chemical shifts for ^1H and ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$.

General Procedure for the Synthesis of *N*-Protected Propargylamines

To a stirred solution of propargylamine in CH_2Cl_2 (8 mL) was added a corresponding acyl chloride or a sulfonyl chloride (1.1 equiv.) at 0 °C. Et_3N (1.5 equiv.) was then added *via* a syringe. The reaction mixture was allowed to slowly warm up to room temperature and was stirred for 10 h. The mixture was then washed with a 1 M HCl solution and subsequently with a brine solution. The combined organic layer was dried by anhydrous Na_2SO_4. In most cases analytically pure products were obtained after the solvent was removed. If necessary, further purification was performed by silica gel chromatography using hexane and ethyl acetate in a ratio of 5:1.

General Procedure for Dimerization of *N*-Protected Propargylamines(Table 3 and Table 4)

An *N*-protected propargylamine (0.5 mmol), 2 mol% $[Rh(COD)Cl]_2$, and 4 mol% dppf were weighed into a flask, which was kept under an argon atmosphere. Subsequently, anhydrous CH_2Cl_2 or toluene (1.5 mL) was added *via* a syringe, and the mixture was stirred at room temperature (for CH_2Cl_2) or 80 °C (for toluene) for 15–24 h. The solvent was then removed under reduced pressure and the residue was purified by silica gel column chromatography.



Scheme 1. Proposed mechanism for the cyclization of **9**.

General Procedure for the Au(II)-Catalyzed Cyclization of Enynes (Table 5)

The following procedure was followed to prepare compounds **18**–**31**. The corresponding enyne (0.5 mmol) and $AuCl_3$ (4.5 mg, 3 mol%) were weighed into a flask in a glove box. CH_2Cl_2 (2 mL) was then slowly added at thee temperatures indicated in Table 5. The mixture was then stirred for another 40 min to 20 h (see Table 5). Removal of the solvent gave a residue which was purified by silica gel column chromatography.

Acknowledgements

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