Organic LETTERS

Letter

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A General Catalyst for Site-Selective C(sp^3)−H Bond Amination of Activated Secondary over Tertiary Alkyl C(sp^3)−H Bonds

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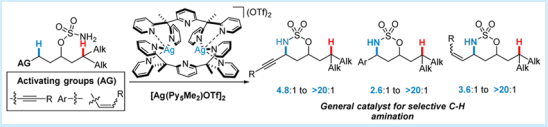
Supporting Information

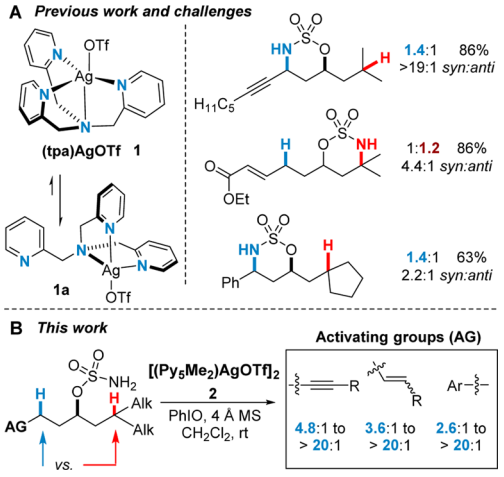
ABSTRACT: The discovery of transition metal complexes capable of promoting general, catalyst-controlled and selective carbon−hydrogen (C−H) bond amination of activated secondary C−H bonds over tertiary alkyl C(sp^3)−H bonds is challenging, as substrate control often dominates when reactive nitrene intermediates are involved. In this letter, we report the design of a new silver complex, [(Py$_5$Me$_2$)AgOTf]$_2$, that displays general and good-to-excellent selectivity for nitrene insertion into propargylic, benzylic, and allylic C−H bonds over tertiary alkyl C(sp^3)−H bonds.



Carbon−nitrogen bonds are ubiquitous in molecules of biological and therapeutic importance. Metal-catalyzed nitrene insertion into C−H bonds[1] represents a streamlined process for the preparation of amine functionality; however, high and predictable chemoselectivity and site selectivity in nitrene transfer are largely a result of substrate control. Thus, there remains strong interest in the development of more versatile catalysts for C−H amination. Despite the broad array of transition metals known to catalyze nitrene transfer,[2−8] a general catalyst for the selective amination of diverse activated secondary C(sp^3)−H bonds in the presence of competing tertiary C(sp^3)−H sites has not yet been identified, particularly when propargylic C−H activation is desired. To address this need, we have designed a new silver complex, [(Py$_5$Me$_2$)AgOTf]$_2$ (Py$_5$Me$_2$ = 2,6-bis[1,1-bis(2-pyridyl)ethyl]pyridine), that exhibits good-to-excellent selectivity for the amination of activated secondary C−H bonds, including propargylic, allylic, and benzylic, even in the presence of competing electron-rich, tertiary C(sp^3)−H sites.

Two features of Ag(I) complexes make them amenable to development as general and selective amination catalysts.[9] The first is the ability of Ag(I) to accommodate diverse coordination geometries at the metal center, from linear to octahedral.[10] Changes in the coordination geometry at Ag can be manipulated through ligand choice, counteranion, solvent, and Ag/ligand ratio to impact the behavior of nitrene transfer. A second feature is the dynamic behavior of Ag(I) complexes in solution. While this was advantageous in achieving highly chemoselective nitrene transfer,[9a] dynamic behavior caused significant complications in our efforts (Scheme 1A)[9b] to attain broad site selectivity for the amination of propargylic, benzylic, and allylic C−H groups over tertiary alkyl C(sp^3)−H bonds. Unfortunately, both steric and electronic modifications to our previous (tpa)AgOTf **1** (tpa = tris(2-pyridylmethyl)amine) catalyst did not improve the selectivities. We surmised these failures were due to dissociation of one or more of the pyridine 'arms' from the metal center of **1**, resulting in the presence of multiple potential catalytic species in solution, including **1** and **1a** (Scheme 1A). In addition, the conformational mobility of **1** could limit its ability to productively discriminate between two competing reactive C−H bonds. Indeed, VT-NMR studies in CD_2Cl_2 over a range of +24 °C to −90 °C supported the presence of dynamic behavior between **1** and **1a** (see the Supporting Information (SI) for more details).

Scheme 1. A General Catalyst for the Amination of Secondary, Activated C−H Bonds over Competing Tertiary Alkyl C−H Bonds

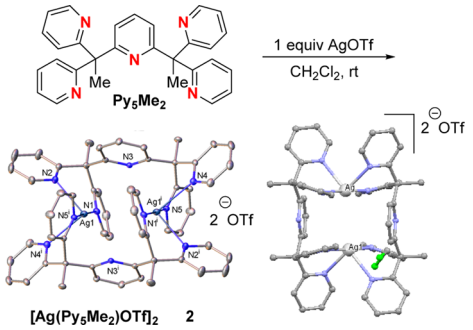


The variability in coordination geometry at the metal center and the dynamic behavior of (tpa)AgOTf **1** prompted us to consider other ligand designs. Efforts to rigidify **1** did not result in general selectivity; thus, we sought a bridging, modular ligand scaffold that could support a potential dimeric silver complex with decreased conformational flexibility. With this design principle in mind, a series of multidentate nitrogenated ligands for Ag(I) were explored, leading to the discovery of a new Ag complex, [(Py$_5$Me$_2$)AgOTf]$_2$ **2** (Scheme 1B and Table 1, bottom).[12] In contrast to **1**, **2** is dimeric in its resting state in both the solid and solution states, as judged by X-ray and DOSY NMR

Received: May 12, 2016

DOI: 10.1021/acs.orglett.6b01392
Org. Lett. XXXX, XXX, XXX−XXX

Table 1. X-ray and DOSY NMR Studies of 2



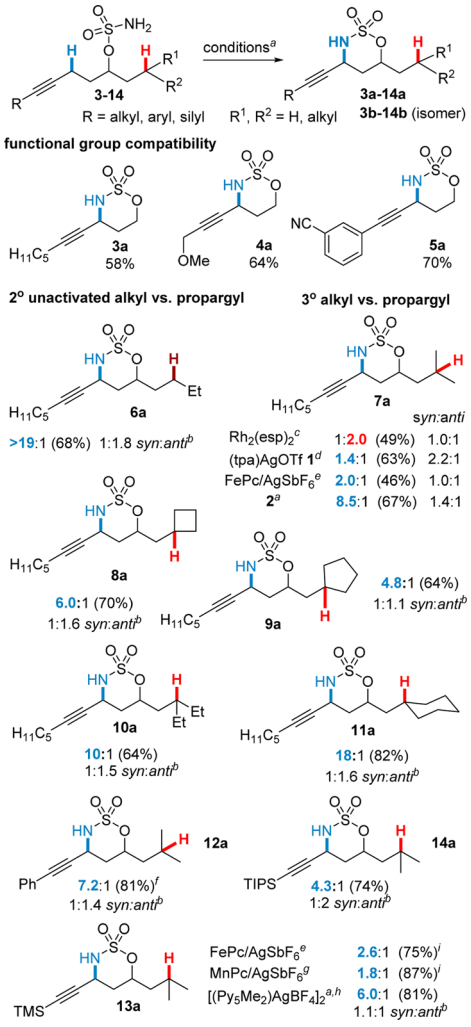
complex	molecular weight (g/mol)	diffusion constant ($\times 10^{-10}$ m^2/s)
lMesAuCl[a]	536.85	11.15
$Rh_2(esp)_2$[a]	758.47	8.436
$Rh_2(TPA)_4$[b]	1355.16	6.976
1[c]	547.30 monomeric	**8.763**
	1094.60 dimeric	
2[c]	700.49 monomeric	**7.074**
	1400.98 dimeric	

[a]0.025 M in CD_2Cl_2. [b]0.0125 M solution in CD_2Cl_2. [c]0.025 M solution based on AgOTf.

studies, respectively (Table 1, top). Each of the Ag atoms in the dimer exhibits a seesaw geometry; the 3.9 Å distance between the two Ag atoms, in combination with the ligand scaffold, forms a restricted 'pocket' where the nitrene precursor could bind. We hypothesized the bridging pyridines of **2** would provide sufficient steric discrimination between activated methylene C−H bonds and sterically hindered, yet more electron-rich, tertiary alkyl C(sp^3)−H bonds.

Complex $[(Py_5Me_2)AgOTf]_2$ **2** was tested against a panel of alkynes (Scheme 2) to determine if it was a competent catalyst for the competitive amination of propargylic C−H bonds. The primary sulfamates **3**−**5** furnished **3a**−**5a** as the major products, showing heteroatom-containing alkynes, including methoxymethyl (**4**) and nitrile (**5**) groups, could tolerate the reaction conditions. Reaction of **6** gave complete preference for amination of the propargylic C−H bond over an unactivated 2° C−H bond, a result expected to display broad scope. Substrates where a tertiary alkyl C(sp^3)−H bond competes with the propargylic C−H bond (Scheme 2, **7**−**14**) have posed difficulties for other nitrene transfer catalysts; Rh-based complexes usually engage with the alkyne, while first-row transition catalysts show approximately statistical selectivities.[7a,13] For example, **7** yielded preferred amination of the tertiary C−H bond to furnish **7b** using $Rh_2(esp)_2$. Our initial (tpa)AgOTf catalyst delivered the desired **7a** as the major product, albeit in a poor 1.4:1 selectivity. An Fe catalyst supported by a phthalocyanine ligand (FePc), in combination with an equimolar amount of $AgSbF_6$, increased this to 2:1.[7a] To our delight, **2** proved to be superior for aminating the propargylic C−H bond, delivering **7a**:**7b** in a ratio of 8.5:1. The scope of the amination with **2** encompassed alkyl, aryl, and silyl substitution at the alkyne, as well as a range of tertiary alkyl substitutions to yield **8a**−**14a** in good-to-excellent selectivities. In general, selectivity at the propargylic C−H site increased as steric bulk around the tertiary C−H bond was increased (compare **8a** to **10a** and **9a** to **11a**). Useful silyl functionalities were tolerated in the reaction, as demonstrated by the syntheses of **13a** and **14a**. The steric bulk of the bridging ligands may also exhibit a remote effect on the

Scheme 2. Site-Selective Propargylic C−H Amination



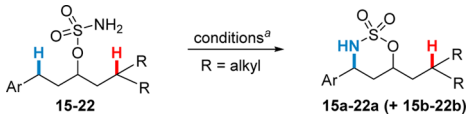
[a]10 mol % AgOTf, 12 mol % Py_5Me_2, 3.5 equiv of PhIO, 0.05 M CH_2Cl_2, 4 Å MS, rt, 30 min. [b]Determined by crude NMR. [c]2 mol % Rh_2esp_2, 1.1 equiv of $PhI(OAc)_2$, 0.16 M CH_2Cl_2, 4 Å MS, reflux, 24 h. [d]10 mol % AgOTf, 12 mol % tpa, 3.5 equiv of PhIO, 0.05 M CH_2Cl_2, 4 Å MS, rt, 30 min. [e]10 mol % [FePc]Cl, 10 mol % $AgSbF_6$, 2.0 equiv of $PhI(OPiv)_2$, 4:1 PhMe/MeCN, ratio of isolated products. [f]Average of two runs. [g]10 mol % [MnPc]Cl, 10 mol % $AgSbF_6$, 2.0 equiv of $PhI(OPiv)_2$, 100 mg of 4 A MS, 9:1 C_6H_6/MeCN, ratio of isolated products. [h]10 mol % $AgBF_4$ found to effect less deprotection of TMS than AgOTf. [i]Reference 7a: *dr* unreported.

selectivity; the TMS group of **13** resulted in better selectivity than the bulky TIPS group of **14**.

$[(Py_5Me_2)AgOTf]_2$ **2** was then tested for the selective amination of benzylic C−H bonds over tertiary alkyl C(sp^3)−H bonds (Table 2). The sensitivity of **2** to the steric environment of the tertiary alkyl C(sp^3)−H bond was apparent in the increased preference for benzylic C−H amination as the bulk of substituents at the tertiary carbon was increased (compare entry 1 with entries 6, 11, and 13−15). Even in cases where the steric hindrance at the tertiary alkyl C(sp^3)−H was lessened due to a 'pinning back' of the alkyl groups, as in **18** and **19**, the use of **2** essentially doubled the selectivity compared to **1** (entries 7 vs 8 and 10 vs 11). Interestingly, both **1** and **2** exhibit similar behavior in the presence of a radical inhibitor (see Table 4, entries 3−4), suggesting that benzylic selectivity is not a result of forming a long-lived radical intermediate, as is the case with most Fe-based

DOI: 10.1021/acs.orglett.6b01392
Org. Lett. XXXX, XXX, XXX−XXX

Table 2. Selectivity for Benzylic C−H Amination with 2



major product	entry	catalyst[a]	a:b	yield (%)	*syn:anti*
15a	1	**2**	2.6:1	80	>20:1
	2	$[Rh_2(esp)_2]^b$	1:7	---	
	3	$[Ru_2(hp)_4Cl]^b$	1.5:1	---	
	4	$FePc/AgSbF_6{}^c$	10:1	56	
Ar = *p*MeOC$_6$H$_4$ **16a**	5	**2**	6.5:1	56	>20:1
17a	6	**2**	7.1:1	62	>20:1
18a	7	**1**[d]	1.4:1	86	>20:1
	8	**2**	3.1:1	95	>20:1
	9	$FePc/AgSbF_6{}^c$	>20:1	36	>20:1
19a	10	**1**[d]	3.7:1	93	>20:1
	11	**2**	7.6:1	95	>20:1
	Ar				
20a	12	Ph $[Rh_2(esp)_2]^b$	1.0:1	65	2.8:1
20a	13	Ph **2**	>20:1	77	>20:1
21a	14	*p*MeOC$_6$H$_4$ **2**	>20:1	62	>20:1
22a	15	*p*F$_3$CC$_6$H$_4$ **2**	9.0:1	50	>20:1

[a]Unless otherwise indicated, the reaction conditions were 5 mol % catalyst **2**, PhIO, 4 A MS, CH_2Cl_2, rt. [b]2.5 mol % $[M_2L_n]$, $PhI(OPiv)_2$, 5 A MS, CH_2Cl_2, 40 °C. [c]10 mol % [FePc]Cl, 10 mol % $AgSbF_6$, 2.0 equiv of $PhI(OPiv)_2$, 4:1 PhMe/MeCN. [d]10 mol % (tpa)AgOTf **1** was employed instead of catalyst **2**.

catalysts giving better selectivity, but lower yields (entries 4, 9).[4] If the tertiary alkyl C−H bond was hindered enough, as in **20**−**22** (entries 13−15), the selectivity for benzylic amination with **2** was excellent, in contrast to the 1:1 mixture observed with $[Rh_2(esp)_2]$ (entry 12). The observed *dr* was high in all cases, favoring the *syn* diastereomer in ratios >20:1 and was attributed to the larger size of the Ph group as compared to the alkyne. This steric bulk enforces a transition state where both the Ph group and the side chain occupy pseudoequatorial positions, leading to preferred formation of the *syn* diastereomer.

Substrates containing an alkene moiety present the additional test of chemoselectivity (Table 3). Our previous strategy of increasing the ratio of ligand/AgOTf to favor allylic amination over aziridination was not successful for sulfamates containing competing reactive C−H bonds.[9a] Achieving both chemoselectivity and site selectivity is also challenging for dinuclear Rh and Ru catalysts (entries 1−3); however, $[Ru_2(hp)_4Cl]$ (entry 4) was successful for amination of **23**.[3a] Catalyst **2** showed better chemoselectivity for **23a**, with no trace of aziridine products (entry 5). The lowered preference for allylic C−H amination in *cis*-substituted alkenes (**23** and **24** in entries 5−6), compared to the >20:1 selectivity for the amination of *trans* alkene **25** (entry 7), again highlights the sensitivity of $[(Py_5Me_2)AgOTf]_2$ to steric effects. Catalyst **2** also provided a surprising reversal in site selectivity compared to $[Rh_2(esp)_2]$ and **1** (entries 8 and 10), favoring the difficult amination of the electron-deficient allylic C−H bond of **26** in much better yield (entry 11) compared to $PcFeCl/AgSF_6$ (entry 9).

Table 3. Selectivity for Allylic C−H Amination with 2

major product	entry (catalyst)[a]	a+b:c	a: b:c	yield (%), dr[b]
23a	1 $[Rh_2(esp)_2]^c$	1.3:1	0.8:1:**1.4**	---
	2 $[Ru_2(esp)_2SbF_6]^c$	1:1.2	3.3:1:**5.3**	---
	3 $[Rh_2(hp)_4]^c$	4:1	1.4:1:0.6	---
	4 $[Ru_2(hp)_4Cl]^d$	>20:1	5:1:0	---
	5 **2**	>20:1	6.1:1:0	71, 1.4:1
24a	6 **2**	>20:1	3.6:1:0	99, 2.3:1[e]
25a	7 **2**	>20:1	>20:1:0	66, 1.1:1
26a	8 $[Rh_2(esp)_2]^c$	>20:1	1:4.8:0	81, 3.8:1
	9 $PcFeCl/AgSbF_6{}^f$	>20:1	3.0:1:0	19, 3.0:1
	10 **1**	>20:1	1:1.2:0	86, 4.4:1
	11 **2**	>20:1	1.9:1:0	66, 1.6:1

[a]Unless otherwise indicated, the reaction conditions were 5 mol % catalyst **2**, PhIO, 4 A MS, CH_2Cl_2, rt. [b]*Syn:anti* ratio for allylic insertion as determined by crude NMR. [c]2.5 mol % $[M_2L_n]$, $PhI(OPiv)_2$, 5 A MS, CH_2Cl_2, 40 °C, NMR ratios. [d]2.5 mol % $[M_2L_n]$, $PhI(OPiv)_2$, 5 A MS, CH_2Cl_2, 40 °C. [e]Isomerization from 9:1 *Z:E* to 3:1 was noted. [f]10 mol % [FePc]Cl, 10 mol % $AgSbF_6$, 2.0 equiv of $PhI(OPiv)_2$, 4:1 PhMe/MeCN.

Our previous catalysts, including **1**, promote nitrene transfer through concerted or rapid H atom abstraction (HAA)/radical rebound pathways;[9a,b] evidence for this same behavior was noted in reactions of **12**, **15**, and **24** with **1** (see the SI for details). In contrast, reactions catalyzed by $[(Py_5Me_2)AgOTf]_2$ **2** in the presence of dihydroanthracene (DHA) as a radical inhibitor (Table 4) showed a significant decrease in the yields **12a** and **24a**

Table 4. Radical Inhibitor Studies of Catalysis Promoted by 2[a]

	entry	conditions	yield (%)	a:b
12a	1	**standard**[b]	81	7.3:1
	2	**DHA**[b]	41	8.5:1
15a	3	**standard**	80	2.6:1
	4	**DHA**	82	3.0:1
24a	5	**standard**	66	>19:1
	6	**DHA**	33	>19:1

[a]Conditions: **standard**: 10 mol % AgOTf, 12 mol % ligand, 3.5 equiv of PhIO, 1 g/mmol 4 Å MS, CH_2Cl_2. **DHA**: 10 mol % AgOTf, 12 mol % ligand, 50% DHA, 3.5 equiv of PhIO, 1 g/mmol 4 Å MS, 0.05 M CH_2Cl_2. [b]Average of two runs.

with DHA (entries 2 and 6) compared to those observed under the standard conditions (entries 1 and 5), suggesting an HAA pathway. Interestingly, **15** furnished similar results in the absence and presence of DHA (entries 3−4), highlighting the subtle interplay between substrate and catalyst in determining the probable mechanism of the nitrene transfer event.

In summary, $[(Py_5Me_2)AgOTf]_2$ **2** was identified as a new catalyst that exhibits a broad preference for the selective amination of propargylic, benzylic, and allylic C−H bonds over

DOI: 10.1021/acs.orglett.6b01392
Org. Lett. XXXX, XXX, XXX−XXX

more electron-rich tertiary alkyl C(sp^3)−H bonds. The dimeric nature of $[(Py_5Me_2)AgOTf]_2$, coupled with increased steric bulk around the metal center, was the key design principle driving the design of this inexpensive and general amination catalyst. Future efforts will focus on continuing to explore the generality of **2**, as well as mechanistic studies to understand the influence of catalyst structure on the pathway of nitrene transfer.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b01392.

Experimental procedures and characterization data for all new compounds, including X-ray crystallographic data for **2** (PDF)

NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was funded through the NSF-CAREER Award 1254397 and the Wisconsin Alumni Research Foundation to J.M.S. Dr. Charles Fry (University of Wisconsin—Madison) is thanked for assistance with NMR spectroscopy. Professor Robert Bergman (University of California—Berkeley) is thanked for helpful comments. The NMR facilities at UW—Madison are funded by the NSF (CHE-9208463, CHE-9629688) and NIH (RR08389-01). The National Magnetic Resonance Facility at Madison is supported by the NIH (P41GM103399, S10RR08438, S10RR029220) and the NSF (BIR-0214394).

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DOI: 10.1021/acs.orglett.6b01392
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