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Tunable differentiation of tertiary C–H bonds in intramolecular transition metal-catalyzed nitrene transfer reactions†

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Metal-catalyzed nitrene transfer reactions are an appealing and efficient strategy for accessing tetrasubstituted amines through the direct amination of tertiary C–H bonds. Traditional catalysts for these reactions rely on substrate control to achieve site-selectivity in the C–H amination event; thus, tunability is challenging when competing C–H bonds have similar steric or electronic features. One consequence of this fact is that the impact of catalyst identity on the selectivity in the competitive amination of tertiary C–H bonds has not been well-explored, despite the potential for progress towards predictable and catalyst-controlled C–N bond formation. In this communication, we report investigations into tunable and site-selective nitrene transfers between tertiary C(sp^3)–H bonds using a combination of transition metal catalysts, including complexes based on Ag, Mn, Rh and Ru. Particularly striking was the ability to reverse the selectivity of nitrene transfer by a simple change in the identity of the N-donor ligand supporting the Ag(I) complex. The combination of our Ag(I) catalysts with known Rh_2(II) complexes expands the scope of successful catalyst-controlled intramolecular nitrene transfer and represents a promising springboard for the future development of intermolecular C–H N-group transfer methods.

Transition metal-catalyzed nitrene transfer is a process utilizing transient hyperelectrophilic metal-bound nitrenes for directly converting ubiquitous and classically inert C–H bonds into valuable C–N bonds. Achieving catalyst control using these reactive intermediates has been a major goal of research in homogenous transition-metal catalysis.[1–9] In the presence of multiple competitive reactive sites, such as the situation presented in a substrate containing an alkene and an allylic C–H bond, a variety of transition metal catalysts have been shown to selectively form either aziridine or amine products by exploiting differences in mechanism, substrate bias or ligand control (Fig. 1A).[9a,b] Orthogonal site-selectivity between C–H bonds in different steric or electronic environments can be achieved by exchanging the identity of the transition metal; for example, Mn catalysts favour reaction at benzylic sites, while Rh_2L_n catalysts favour a 3° methine (Fig. 1B).[2h,7a] In this work, we expand the utility of metal-catalyzed nitrene transfer to encompass tunable amination of competing 3° C–H bonds in similar steric and/or electronic environments using a combination of ligand-controlled Ag(I) catalysis and scaffolds based on other metals (Fig. 1C). A better understanding of how interactions between substrate and catalyst selectively differentiate 3° C–H bonds enables development of 2nd-generation catalysts that install a C–N bond at a desired site in a complex molecule setting.

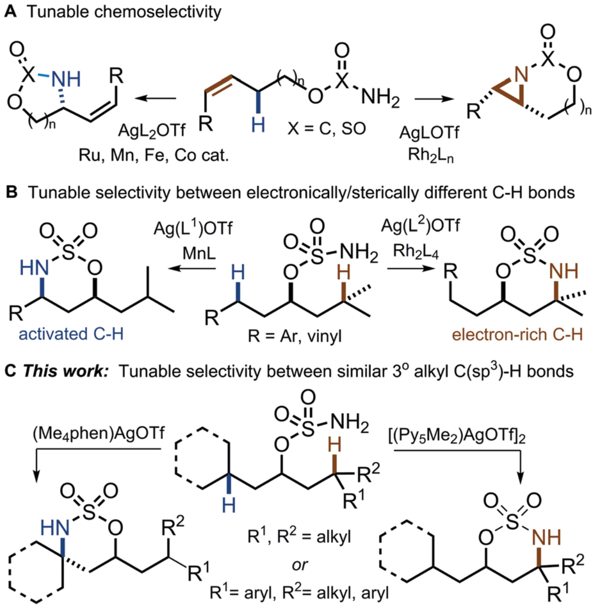

Fig. 1 Catalyst control in intramolecular metal–nitrene transfer.

Examples of differentiating between aminations of competing 3° C–H bonds are scarce and no tunable examples have been reported.[2h,7a,9b] The Du Bois group has shown that the treatment of **1** with either $Rh_2(OAc)_4$ ($\mathbf{1_{iPr}:1_{cHex}}$ 2.0 : 1)[2h] or $Rh_2(TPA)_4$ **5**

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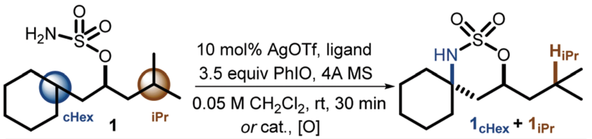
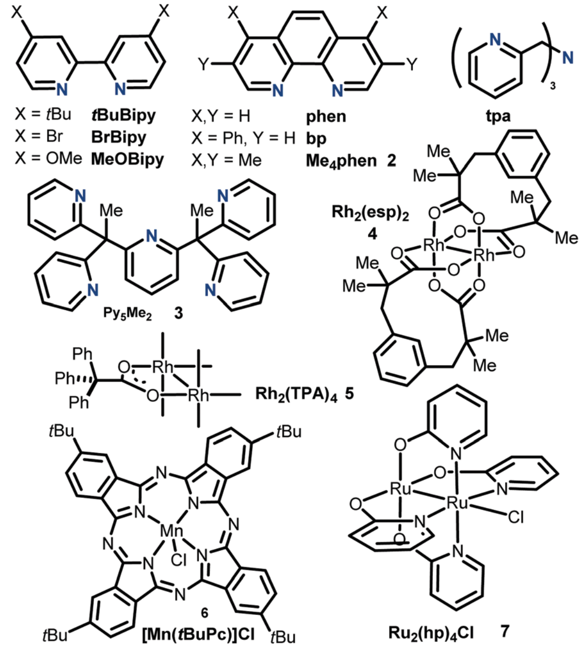
Table 1 Differentiation between similar tertiary C(sp^3)–H bonds



entry	lig/cat	Ag:L	yield[a]	cHex : *iPr*	entry	lig/cat[b]	Ag:L	yield[a]	cHex : *iPr*
1	BrBipy	1:3	38%	**1.6** : 1	7	tpa	1:1.25	99%	1 : **1.4**
2	*t*BuBipy	1:3	91%	**3.5** : 1	8	**3**	1:1.25	97%	1 : **3.9**
3	MeOBipy	1:3	91%	**4.5** : 1	9	**4**	-	98%	1 : **4.3**
4	phen	1:3	97%	**3.8** : 1	10	**5**	-	85%	1 : **6.0**
5	bp	1:3	96%	**4.1** : 1	11	**6**	-	46%	1 : **4.1**
6	**2**	1:1.25	95%	**5.0** : 1	12	**7**	-	88%	1 : **3.3**



[a] NMR yield, mesitylene internal standard. [b] See the ESI for conditions using catalysts **4–7**. The reactions were run to complete conversion of the substrate **1**.

(Table 1, entry 10) favours reaction at the 3° **iPr** over the 3° **cHex** C–H bond, presumably due to greater $\sigma_{\text{C–H}} \rightarrow \sigma_{\text{C–H}}{}^*$ at **iPr**, rendering that site more electron-rich. Selectivity for $\mathbf{1_{iPr}}$ increases from 2.0 : 1 to 4.3 : 1 to 6 : 1 in moving from OAc to $Rh_2(esp)_2$ (entry 9) to the bulky and less electron-rich triphenylacetate (TPA) ligand for the Rh_2(II) catalyst.

Investigations of a series of our Ag(I) catalysts (Table 1, entries 1–8) yielded interesting and unexpected results. A control reaction employing AgOTf and no ligand gave <3% of the aminated products in a ~1 : 1 ratio of $\mathbf{1_{cHex}}$: $\mathbf{1_{iPr}}$. More electron-rich 2,2′-bipyridine (bipy) ligands (compare entries 2–3 with entry 1) gave better selectivity and higher yields for $\mathbf{1_{cHex}}$. More rigid 1,10-phenanthroline-based (phen) ligand scaffolds (entries 4–6), especially the electron-rich Me_4phen (entry 6), also exhibited selectivity for $\mathbf{1_{cHex}}$.

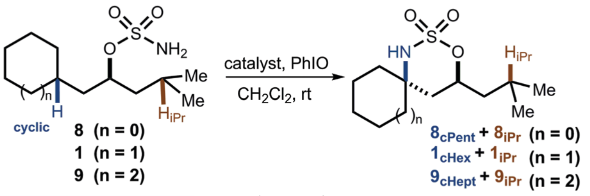
Switching to a tris(2-pyridylmethyl)amine (tpa) ligand (entry 7) resulted in a modest switch in site-selectivity to favour $\mathbf{1_{iPr}}$. A dimeric Ag catalyst based on **3** (entry 8) further improved selectivity for $\mathbf{1_{iPr}}$, accomplishing tunable, catalyst-controlled nitrene transfer using a single metal (compare entries 6 and 8).

The reasons for the tunability between the **iPr** and **cHex** C–H bonds of **1** were not readily apparent. [Mn(*t*BuPc)]Cl **6** and $Ru_2(hp)_4Cl$ **7** promote step-wise nitrene transfer pathways and also favour amination of the 3° **iPr** C–H bond of **1** (entries 11–12).[3a] This is intriguing, as Rh_2(II) catalysts engage in concerted intramolecular nitrene transfer, yet show the same overall site-selectivity as **6–7**. The mechanism of Ag(I)-catalyzed nitrene transfer is necessarily step-wise, due to the lack of a vacant π* orbital on the N of the metal nitrene.[9d] However, we and others have shown that the nature of the ligand on Ag can impact whether the amination proceeds through HAT involving discrete radical intermediates, or undergoes a barrierless radical rebound that results in 'concerted-like' behaviour in the nitrene transfer.[8,9] This is reflected in the very different selectivities between catalysts **2** and **3**. Thus, rationalizing subtle differences in site-selectivity by invoking a broad picture of the mechanism of nitrene transfer cannot be applied in the same way as previous reports of chemoselective nitrene transfer (Fig. 1A). Rather, subtle interactions between ligand architecture, substrate and catalyst electronics all play important, but poorly understood, roles in fine-tuning the steric and electronic environment of the metal–nitrene.

To gain further insight into the factors most important in influencing selectivity of nitrene transfer in these types of systems, substrates **8** and **9** were explored (Table 2) with catalysts **2–7**. Despite the observation that tunability could be achieved using ligand-controlled Ag(I) catalysis or by switching the metal identity, no trends in the selectivity were immediately apparent, requiring a more careful analysis of the interplay between the features of the substrate (electron density, C–H bond dissociation energy (BDE) and *A*-value of the alkyl group) and the catalyst (KIE, mechanism of nitrene transfer).

Catalysts with reported KIE values in the range of ~0–4, such as the dinuclear Rh_2(II) paddlewheel catalysts **4–5**, are thought to proceed through concerted nitrene transfer and favor the most electron-rich C–H bond (Fig. 2A, reactivity trend: 3° > ethereal ≈ benzylic > 2° ≫ 1°).[2] Catalysts with KIEs > 4, as represented by **6** (KIE = 4.2) and **7** (KIE = 4.9), favour reaction at the weakest C–H bond (Fig. 2A, reactivity trend: allylic > benzylic > ethereal > 3° > 2° ≫ 1°) due to the preference for a step-wise nitrene transfer

Table 2 Selectivity in the amination of carbocyclic *vs.* acyclic C–H bonds



entry	n, Cy	cat.[a]	yield[b]	Cy : *iPr*	n = 1	entry	n, Cy	cat.[a]	yield[b]	Cy : *iPr*
1	0, *c*Pent	**2**	93%	**2.5** : 1	**5.0** : 1	7	2, *c*Hept	**2**	96%	**7.3** : 1
2	0, *c*Pent	**3**	87%	**1.8** : 1	1 : **3.9**	8	2, *c*Hept	**3**	96%	**1.3** : 1
3	0, *c*Pent	**4**	98%	**1.3** : 1	1 : **4.3**	9	2, *c*Hept	**4**	96%	**1.2** : 1
4	0, *c*Pent	**5**	84%	1 : **2.1**	1 : **6.0**	10	2, *c*Hept	**5**	96%	1 : **2.1**
5	0, *c*Pent	**6**	56%	1 : **2.6**	1 : **3.3**	11	2, *c*Hept	**6**	51%	1 : **1.2**
6	0, *c*Pent	**7**	65%	1.0 : 1	1 : **4.1**	12	2, *c*Hept	**7**	78%	**2.1** : 1

[a] See the ESI for detailed reaction conditions using catalysts **2–7**. [b] NMR yield, mesitylene internal standard. The reactions were run to complete conversion of the substrate.

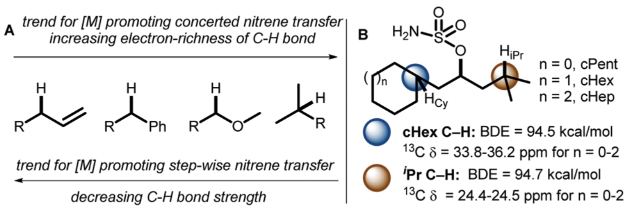


Fig. 2 Traditional substrate control explanations of site-selectivity fail when similar logic is applied to tertiary C(sp^3)–H differentiation.

pathway involving radical intermediates with significant lifetimes.[3a,4c,7a] The two 3° C–H bonds of **1**, **8** and **9** have essentially the same BDEs, but the isopropyl C–H appears to be more electron-rich than the Cy C–H bonds, according to comparisons of the ^{13}C chemical shifts (Fig. 2B). An additional factor to consider is the conformational flexibility of the Cy ring; while **cHex** is likely to favour a distinct chair conformation, the flexibility of cPent and cHept may make the cyclic C–H bond more difficult to differentiate from an acyclic C–H bond.

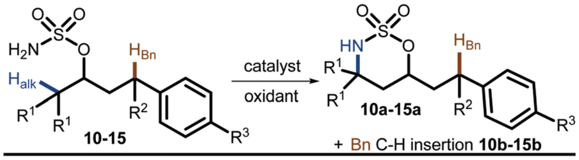
If we consider the selectivity exhibited for **1** using **2–7**, it is apparent that Rh_2(II) complexes **4–5** favour the more electron-rich **iPr** C–H, as expected. Concerted C–H insertion reactions catalysed by Rh_2(II) complexes are proposed to proceed through triangular, three-membered transition states that show a steric preference for approaching an equatorial C–H over one in the axial position in the **cHex** ring.[1,2] In addition, equatorial C–H bonds are more deshielded than axial ones due to anisotropic effects, an effect that further exacerbates the tendency for amination at the **iPr** C–H (Table 1, entries 9 and 10). In contrast, the conformational flexibility of the cPent and cHept groups in **8–9** may lower the site-selectivity, although $Rh_2(TPA)_4$ **5** (Table 2, entries 4 and 10) does display a greater sensitivity to electronics as compared to $Rh_2(esp)_2$ **4** (entries 3 and 9). This may be due to the relatively electron-poor TPA carboxylate resulting in a Rh–nitrene with increased electrophilicity.

In contrast to catalysts that promote concerted nitrene transfer, stepwise reactions proceed through H-atom transfer (HAT) transition states that lead to radical intermediates displaying a linear N···H···C geometry, resulting from three-center/three-electron or three-center/four-electron bonds.[1,9d] As shown in Fig. 2A, these catalysts rely in differences in BDE to enable predictable preference for one C–H bond over another. Indeed, catalysts **6–7** showed poor selectivity in differentiating conformationally fluxional tertiary C–H bonds in **8–9** (Table 2, entries 5, 6 and 11, 12). Use of **6** resulted in the more electron-rich carbon radical leading to $\mathbf{8_{iPr}}$ (entry 11), but this is not always a selectivity-determining feature, as **7** led to formation of $\mathbf{9_{Cy}}$ (entry 12). Using the trends in Rh, Ru and Mn catalysis to understand the behaviour of Ag catalysts **2–3** was instructive. It is worth noting that **3** (Table 1, entry 3 and Table 2, entries 2 and 8) displays similar behaviour to **6–7**, implying that this Ag(I) complex proceeds through a nitrene transfer involving HAT and formation of long-lived radical intermediates.[3a,7a] Indeed, the KIE for **3** was 5.7, in line with values obtained for **6** (4.2) and **7** (4.9).[3a,4c,7a] The most intriguing results were the observation that $Ag(Me_4phen)OTf$ **2** (Table 1, entry 6 and Table 2, entries 1 and 7) increasingly favoured amination of the **Cy** C–H as the carbocycle increased in size from cPent to cHept, perhaps due to the fluxional nature of *c*Hept and the greater rate of pseudo-equatorial C–H bond oxidation by strain release during the amination event.[1]

Previous work in intramolecular nitrene transfer competition experiments generally attributes the preference for the amination of benzylic methylene C–H over 3° alkyl C(sp^3)–H bonds to lower BDEs and stereoelectronic stabilization of the amination transition state (concerted or stepwise) by relatively large $\pi_{C=C} \rightarrow \sigma_{C-H}^*$ interactions.[1,3a,4c,7a,9c] We were curious how a more electronically activated benzylic 3° C–H bond in **10–15** might compete with less activated, but more electron-rich, 3° alkyl C(sp^3)–H bonds (Table 3). We explored three catalysts, **2**, **3** and **5**, that display very different reactivity profiles as determined by our results (Tables 1 and 2).

Substrates **10–12** were designed to compare the activation of a conformationally accessible **cHex** C–H bond with a series of different benzylic methine C–H bonds of decreasing BDE in moving from **10** to **12** (Table 3, entries 1–9). The substrates were utilized as ~1 : 1 mixtures of diastereomers; however, evidence of tunable selectivity in the amination can still be assessed. Further studies to determine how the stereochemistry impacts relative rates of C–H amination are underway and will be reported in due course. The preference of $Ag(Me_4phen)OTf$ **2** for the most conformationally accessible **cHex** C–H bond (entries 1–3) decreased as the Bn C–H bond became weaker. AgOTf supported by Py_5Me_2 in **3** (entries 4–6) showed an increase in selectivity for the Bn C–H bond from 2.2 : 1 to 8.4 : 1 as the BDE was decreased, a trend that fits our mechanistic picture of step-wise nitrene transfer promoted by **3**.[9c] Finally, $Rh_2(TPA)_4$ **5** (entries 7–9) responded to decreased electron density at the C–H bond by heavily favouring the **cHex** C–H bond in **12** (entry 9). Somewhat surprising was the lack of

Table 3 Competitive amination of activated C–H *vs.* 3° C(sp^3)–H bonds



R¹, R², R³		R¹, R², R³		R¹, R², R³	
-$(CH_2)_5$-, Me, H	**10**	-$(CH_2)_5$-, Ph, H	**12**	Me, Me, OMe	**14**
-$(CH_2)_5$-, Me, OMe	**11**	Me, Me, H	**13**	Me, Ph, H	**15**

entry	substrate	cat[a]	yield[b]	Alk:Bn (a:b)	entry	substrate	cat[a]	yield[b]	Alk:Bn (a:b)
1	**10**	**2**	95%	**3.8** : 1					
2	**11**	**2**	90%	**2.2** : 1	10	**13**	**2**	89%	1 : **1.3**
3	**12**	**2**	83%	**1.2** : 1	11	**14**	**2**	73%	1 : **2.6**
4	**10**	**3**	84%	1 : **2.2**	12	**15**	**2**	89%	1 : **4.2**
5	**11**	**3**	89%	1 : **3.4**	13	**13**	**3**	91%	**1.0** : 1
6	**12**	**3**	81%	1 : **8.4**	14	**14**	**3**	90%	1 : **1.4**
7	**10**	**5**	93%	1 : **1.1**	15	**15**	**3**	83%	1 : **2.7**
8	**11**	**5**	92%	1 : **1.8**	16	**13**	**5**	94%	**8.3** : 1
9	**12**	**5**	70%	**>19** : 1	17	**15**	**5**	93%	**>19** : 1

[a] See the ESI for conditions using catalysts **2–5**. [b] NMR yield, mesitylene internal standard. The reactions were run to complete conversion of the substrate.

selectivity in **10** with **5** (entry 7), reflecting either similar electron density around the two 3° C–H bonds or a steric component to the site-selectivity.

The effect of the conformational accessibility of a **cHex** C–H bond was removed in **13–15**, where amination of a series of 3° benzylic methine C–H bonds were compared to an **iPr** C–H bond (Table 3, entries 10–17). Ag(Me$_4$phen)OTf **2** showed increased selectivity for the Bn C–H bond in moving from **13** to **15**, rationalized by adoption of a preferred conformation about the hindered and activated **Bn** C–H to maximize π-C–H* interactions. This suggests **2** favours kinetically accessible C–H bonds to a greater extent than the other catalysts tested in Table 3, an observation previously made with **2** (Table 1). Catalyst **3** displayed less selectivity for **Bn** in **13–15** (entries 13–15) as compared to **10–12** (entries 5–7), suggesting **3** may be more sensitive to the electronics of the C–H bond than the kinetic accessibility. Finally, Rh$_2$(TPA)$_4$ **5** (entries 16 and 17) responded to the increased electron density at the **iPr** C–H.

It is worth noting that both Ag(I) catalysts **2** and **3** favor amination of the diphenyl methine C–H over the **iPr** C–H bond of **15**, even though it is more encumbered (*A*-value of Ph = 3 *vs.* Me = 1.7). It appears increasing the stereoelectronic bias against an acyclic 3° alkyl C–H bond improves the selectivity of Ag(I) catalysts for the activated C–H bond, due to the inherent stepwise nature of nitrene transfer in all Ag(I) catalysts. Thus, Ag(I) complexes are promising scaffolds for developing catalysts that select for any 'activated' 3° C–H bond over a typical 3° alkyl C(sp^3)–H bond. Although Rh$_2$(II) catalysts rely heavily on substrate control, they often favour 3° alkyl C(sp^3)–H bonds, leading to our demonstration of catalyst-controlled tunability between 3° C–H bonds (Table 3, entries 6 *vs.* 9 and 12 *vs.* 17) can be achieved.

In conclusion, we report the first examples of site-selective C–H aminations of substrates containing reactive 3° C–H bonds in similar steric and electronic environments. In many cases, tunability was achieved solely by changing the nature of an N-donor ligand for the Ag(I) complex; however, in challenging substrates, the orthogonal reactive site was favoured using Rh$_2$(TPA)$_4$. Though the underlying mechanistic rationale for differentiating similar C–H bonds is not yet well-understood, achieving this level of catalyst control is promising for future development of site-selective and tunable intermolecular metal–nitrene transfer; a long-standing challenge in the field.

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