Metalloporphyrin-Mediated Asymmetric Nitrogen-Atom Transfer to Hydrocarbons: Aziridination of Alkenes and Amidation of Saturated C–H Bonds Catalyzed by Chiral Ruthenium and Manganese Porphyrins

Jiang-Lin Liang, Jie-Sheng Huang, Xiao-Qi Yu, Nianyong Zhu, and Chi-Ming Che*[a]

Abstract: Chiral metalloporphyrins [Mn(Por*)(OH)(MeOH)] (**1**) and [Ru(Por*)(CO)(EtOH)] (**2**) catalyze asymmetric aziridination of aromatic alkenes and asymmetric amidation of benzylic hydrocarbons to give moderate enantiomeric excesses. The mass balance in these nitrogen-atom-transfer processes has been examined. With PhI=NTs as the nitrogen source, the aziridination of styrenes, *trans*-stilbene, 2-vinylnaphthalene, indene, and 2,2-dimethylchromene catalyzed by complex **1** or **2** resulted in up to 99% substrate conversions and up to 94% aziridine selectivities, whereas the amidation of ethylbenzenes, indan, tetralin, 1-, and 2-ethylnaphthalene catalyzed by complex **2** led to substrate conversions of up to 32% and amide selectivities of up to 91%. Complex **1** or **2** can also catalyze the asymmetric amidation of 4-methoxyethylbenzene, tetralin, and 2-ethylnaphthalene with "$PhI(OAc)_2 + NH_2SO_2Me$", affording the N-substituted methanesulfonamides in up to 56% *ee* with substrate conversions of up to 34% and amide selectivities of up to 92%. Extension of the "complex **1** + PhI=NTs" or "complex **1** + $PhI(OAc)_2 + NH_2R$ (R = Ts, Ns)" amidation protocol to a steroid resulted in diastereoselective amidation of cholesteryl acetate at the allylic C–H bonds at C-7 with substrate conversions of up to 49% and amide selectivities of up to 90% (α:β ratio: up to 4.2:1). An aziridination- and amidation-active chiral bis(tosylimido)ruthenium(VI) porphyrin, [Ru(Por*)$(NTs)_2$] (**3**), and a ruthenium porphyrin aziridine adduct, [Ru(Por*)(CO)(TsAz)] (**4**, TsAz = *N*-tosyl-2-(4-chlorophenyl)aziridine), have been isolated from the reaction of **2** with PhI=NTs and *N*-tosyl-2-(4-chlorophenyl)aziridine, respectively. The imidoruthenium porphyrin **3** could be an active species in the aziridination or amidation catalyzed by complex **2** described above. The second-order rate constants for the reactions of **3** with styrenes, 2-vinylnaphthalene, indene, ethylbenzenes, and 2-ethylnaphthalene range from 3.7–42.5×10^{-3} $dm^3 mol^{-1} s^{-1}$. An X-ray structure determination of complex **4** reveals an O- rather than N-coordination of the aziridine axial ligand. The fact that the *N*-tosylaziridine in **4** does not adopt an N-coordination mode disfavors a concerted pathway in the aziridination by a tosylimido ruthenium porphyrin active species.

Keywords: amidation · asymmetric catalysis · aziridination · manganese · porphyrinoids · ruthenium

Introduction

Metalloporphyrin-mediated hydrocarbon functionalization is of particular importance in biomimetic investigation and is potentially useful in organic synthesis. The epoxidation,[1] aziridination,[2] and cyclopropanation[3] of alkenes and the hydroxylation[4] and amidation[2e, 5] of saturated C–H bonds are among the most common hydrocarbon-functionalization reactions mediated by a metalloporphyrin, which are widely believed to proceed by oxygen-, nitrogen-, and carbon-atom transfer from oxo-, imido-, and carbene-metalloporphyrin active species, respectively (Scheme 1). Despite the current absence of practical metalloporphyrin catalysts, metalloporphyrin-catalyzed hydrocarbon-functionalization reactions remain attractive not only because of their unique relationship to heme-containing enzymes but also because of their unusually high selectivity and catalyst turnover numbers observed in many cases. To extend the utility of metalloporphyrin catalysts to asymmetric synthesis, a wide variety of chiral metalloporphyrins have been developed[1b] and their catalytic behavior toward asymmetric hydrocarbon-functionalization reactions by oxygen- and carbon-atom-transfer processes has been extensively investigated.[1a–j, 3b,d,j–l,n,p, 4c,g] However, little is known about the catalytic properties of a chiral metalloporphyrin for asymmetric hydrocarbon-functionalization reactions by nitrogen-atom-transfer processes.

Recently, we initiated exploration of chiral metalloporphyrins as catalysts for asymmetric nitrogen-atom-transfer reactions and preliminarily reported the aziridination of

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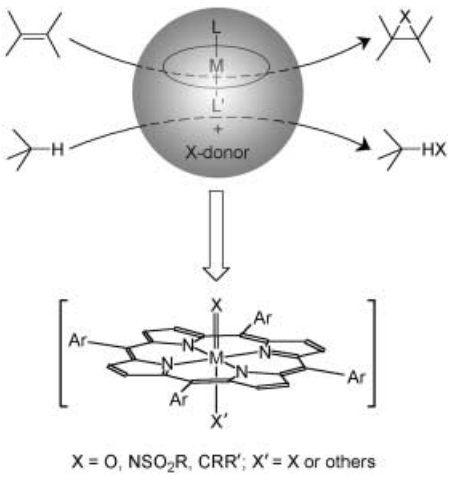
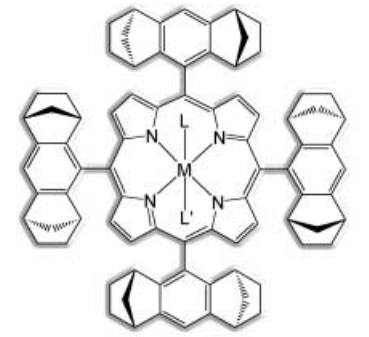


Scheme 1. Common metalloporphyrin-mediated hydrocarbon-functionalization reactions by oxygen-, nitrogen-, and carbon-atom transfer from putative metal-oxo, -imido, and -carbene active species (X = O, NSO_2R, and CRR′, respectively).

aromatic alkenes with iminoiodane PhI=NTs in the presence of chiral manganese porphyrin [Mn(Por*)(OH)(MeOH)] (**1**) (which afforded *N*-tosylaziridines in up to 76% yield with up to 68% *ee*)[6] and the PhI=NTs amidation of benzylic hydrocarbons in the presence of **1** or chiral ruthenium porphyrin [Ru(Por*)(CO)(EtOH)] (**2**) (which afforded *N*-substituted toluenesulfonamides in up to 54% *ee*).[7] These, together with



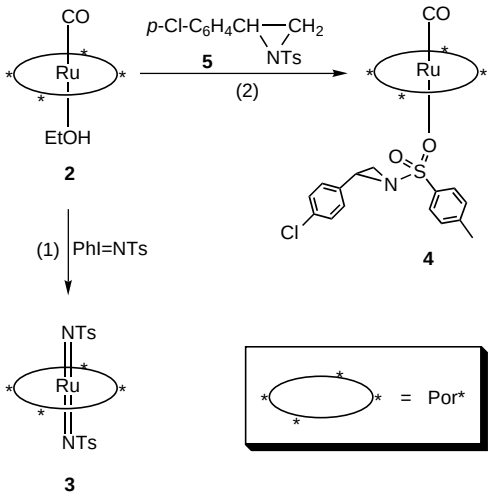
	M	L	L'
1	Mn	OH	MeOH
2	Ru	CO	EtOH
3	Ru	NTs	NTs
4	Ru	CO	*p*-Cl-C_6H_4CH(NTs)—CH_2

subsequent work by Marchon and co-workers on the PhI=NR (R = Ts or $SO_2C_6H_4OMe$) aziridination of styrene catalyzed by manganese or iron tetramethylchiroporphyrins (which afforded *N*-tosylaziridines in up to 34% yield with up to 57% *ee*),[8] are so far the only reports in the literature concerning *asymmetric* nitrogen-atom-transfer reactions mediated by a metalloporphyrin. Both **1** and **2** consist of a sterically demanding D_4-symmetric chiral porphyrin ligand 5,10,15,20-tetrakis-{(1*S*,4*R*,5*R*,8*S*)-1,2,3,4,5,6,7,8-octahydro-1,4:5,8-dimethanoanthracene-9-yl}porphyrin [H_2(Por*)] first synthesized by Halterman and Jan.[9] The amidations of benzylic hydrocarbons[7] catalyzed by complex **1** or **2** are exceedingly rare examples of asymmetric amidation with iminoiodanes catalyzed by a metal complex. The only previous example is the rhodium-catalyzed asymmetric amidation of hydrocarbons with PhI=NNs reported by Müller and co-workers,[10] which afforded amides in up to 31% *ee*.[11]

Herein, we report the first examples of 1) asymmetric aziridination of alkenes catalyzed by a chiral ruthenium porphyrin, 2) asymmetric amidation of saturated C–H bonds with "PhI$(OAc)_2$ + NH_2R" catalyzed by a metal complex, and 3) amidation of a cholesteryl ester with either PhI=NTs or "PhI$(OAc)_2$ + NH_2R" catalyzed by a metalloporphyrin, together with a mass balance study on the **1**- or **2**-mediated aziridination and amidation reactions. To help understand the mechanism in the ruthenium-catalyzed asymmetric nitrogen-atom-transfer reactions, a chiral bis(tosylimido)ruthenium(VI) porphyrin, [Ru(Por*)$(NTs)_2$] (**3**), and a ruthenium porphyrin aziridine adduct, [Ru(Por*)(CO)(TsAz)] (**4**, TsAz = *N*-tosyl-2-(4-chlorophenyl)aziridine), were isolated; the former is the only example of an isolated chiral metalloporphyrin bearing an imido axial ligand and the latter contains an *O-bound N*-tosylaziridine. Kinetic studies were carried out to measure the rate constants for the stoichiometric reactions of **3** with a series of hydrocarbons; the results were compared with those obtained for bis(tosylimido)ruthenium complexes of simple porphyrins[2e] to examine the effect of porphyrin ligands on the ruthenium-porphyrin-mediated nitrogen-atom-transfer reactions.

Results

Synthesis and characterization of chiral ruthenium porphyrins 3 and 4: Treatment of **2** with 4 equiv of PhI=NTs in dichloromethane rapidly produced the bis(tosylimido)ruthenium(VI) porphyrin **3** (reaction (1) in Scheme 2), which was isolated in 64% yield after chromatography on alumina. Note that in our preliminary work[7] complex **3** was generated in situ and not isolated in pure form. The main ^{1}H NMR, UV/Vis, and IR spectral features of **3** resemble those of bis(tosylimido)ruthenium(VI) complexes of other *meso*-tetraarylporphyrins.[2e]



Scheme 2. Synthesis of chiral ruthenium porphyrins **3** and **4**.

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The ruthenium porphyrin **4** was obtained in 85 % yield by treatment of **2** with excess *N*-tosyl-2-(4-chlorophenyl)aziridine (**5**) in chloroform (reaction (2) in Scheme 2). The O- rather than N-coordination mode in **4** was established by X-ray crystallography (see below). To our knowledge, this is the first metalloporphyrin bearing an aziridine axial ligand.[12] As expected, the key spectral features of **4** (including the Soret and β bands in the UV/Vis spectrum, the ν(CO) band in the IR spectrum, and the proton resonances of the porphyrin ligand in the ^{1}H NMR spectrum) are similar to those of **2**. Somewhat surprising is that the ^{1}H NMR signals of the coordinated **5** in **4** in CD_2Cl_2 are very similar to those of free **5** ($\Delta\delta \leq 0.03$ ppm) in the same deuterated solvent. This suggests a liberation of **5** from **4** in the solution.

X-ray crystal structure of ruthenium porphyrin aziridine adduct 4: Figure 1 depicts the structure of **4** with the key atom-numbering scheme. The crystal data and structure

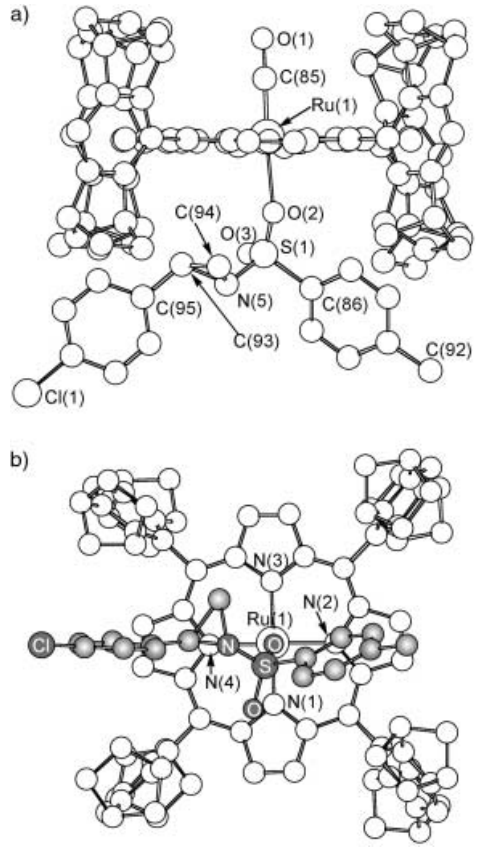


Figure 1. X-ray crystal structure of [Ru(Por*)(CO)(TsAz)] (**4**) with the key atom-numbering scheme viewed along the a) N(3)–N(1) axis and b) O(2)–Ru(1) axis. Hydrogen atoms are not shown and the atoms of the aziridine axial ligand in b) are filled with grey colors.

refinements for **4** are compiled in Table 1; selected bond lengths and angles for the complex are given in Table 2. This ruthenium porphyrin, like complex **2**,[3k] has a distorted octahedral coordination geometry and has an axial Ru–CO moiety featuring an Ru–C(CO) bond length of $\approx$1.76 Å and Ru–C–O angle of $\approx$179°. The porphyrin plane shows a slight saddle distortion and the ruthenium atom is slightly out of the mean porphyrin plane toward the CO axial group.

Table 1. Crystal data and structure refinement for complex **4**.

formula	$C_{100}H_{90}N_5ClO_3RuS$
M_R	1578.35
λ [Å]	0.71073
T [K]	301
crystal system	triclinic
space group	$P1$
a [Å]	10.801(2)
b [Å]	14.220(3)
c [Å]	15.294(3)
α [°]	78.90(3)
β [°]	77.39(3)
γ [°]	84.85(3)
V [Å^3]	2246.7(8)
Z	1
ρ_{calcd} [Mg m^{-3}]	1.167
$\mu(Mo_{K\alpha})$ [mm^{-1}]	0.278
$F(000)$	826
index ranges	$-12 \leq h \leq 11$, $-17 \leq k \leq 16$, $-18 \leq l \leq 18$
reflections collected	13110
independent reflections	11070
refinement method	full-matrix least-squares on F^2
parameters	985
goodness-of-fit	1.059
final R indices	$R_1 = 0.076$, $wR_2 = 0.202$
absolute structure parameter	0.05(4)
largest diff. peak:hole [e Å^{-3}]	1.31/ – 0.59

Table 2. Selected bond lengths [Å] and bond angles [°] for complex **4**.

bond lengths			
Ru(1)–C(85)	1.76(1)	Ru(1)–O(2)	2.256(8)
Ru(1)–N(1)	2.008(9)	Ru(1)–N(2)	2.074(9)
Ru(1)–N(3)	2.07(1)	Ru(1)–N(4)	2.045(9)
C(85)–O(1)	1.18(1)	S(1)–O(2)	1.435(8)
S(1)–O(3)	1.50(1)	S(1)–N(5)	1.59(1)
S(1)–C(86)	1.75(1)	C(93)–C(94)	1.63(2)
N(5)–C(93)	1.46(2)	N(5)–C(94)	1.57(2)
bond angles			
Ru(1)-C(85)-O(1)	179(1)	Ru(1)-O(2)-S(1)	148.0(6)
N(1)-Ru(1)-N(2)	88.9(3)	N(2)-Ru(1)-N(3)	90.2(4)
N(3)-Ru(1)-N(4)	90.2(4)	N(1)-Ru(1)-N(4)	90.2(3)
N(1)-Ru(1)-N(3)	173.9(4)	N(2)-Ru(1)-N(4)	175.2(4)
C(85)-Ru(1)-N(1)	92.5(5)	C(85)-Ru(1)-N(2)	92.9(5)
C(85)-Ru(1)-N(3)	93.6(5)	C(85)-Ru(1)-N(4)	91.9(4)
O(2)-Ru(1)-N(1)	86.8(3)	O(2)-Ru(1)-N(2)	84.2(3)
O(2)-Ru(1)-N(3)	87.1(3)	O(2)-Ru(1)-N(4)	91.0(3)
O(2)-S(1)-C(86)	108.2(6)	O(2)-S(1)-N(5)	112.8(6)
O(2)-S(1)-O(3)	120.4(6)	S(1)-N(5)-C(93)	118.3(9)
S(1)-N(5)-C(94)	113.7(9)	C(93)-N(5)-C(94)	64.7(9)
N(5)-C(93)-C(94)	61.0(9)	N(5)-C(94)-C(93)	54.2(8)

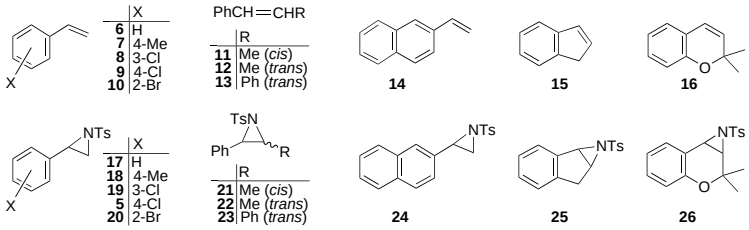
As shown in Figure 1, the aziridine axial ligand **5** in **4** is coordinated to ruthenium by an oxygen atom (O(2)) of the tosyl group rather than by the nitrogen atom of the aziridine ring; the Ru–O(2) bond length of 2.256(8) Å is comparable to the Ru–O(EtOH) bond length of 2.241(1) Å in **2**.[3k] Both the *p*-chlorophenyl and *p*-tolyl groups of **5** lie almost halfway between adjacent norbornane moieties of the porphyrin ligand (see Figure 1b). Compared to structurally characterized free aziridines,[13, 14] the coordinated **5** in **4** has an aziridine ring with some unusual metrical parameters (for example the C(93)–C(94) bond of 1.63(2) Å is rather long). This may result from a disorder of the atoms in the three-membered aziridine ring.

Asymmetric aziridination of aromatic alkenes: *Mass balance in the aziridination catalyzed by complex **1** or **2***: We examined the reactions of a series of aromatic alkenes with PhI=NTs in the presence of ≈1.3 mol% complex **1** or **2**. The reactions were generally performed in dichloromethane at 40 °C for 2 h by employing excess PhI=NTs (catalyst:substrate:(PhI=NTs) molar ratio = 1:75:150) to facilitate assessment of the mass balance in the catalytic processes. Table 3 shows the results obtained for the aziridination of styrene (**6**), 4-methylstyrene (**7**), 3-chlorostyrene (**8**), 4-chlorostyrene (**9**), 2-bromostyrene (**10**), *cis*-β-methylstyene (**11**), *trans*-β-methylstyene (**12**), *trans*-stilbene (**13**), 2-vinylnaphthalene (**14**), indene (**15**), and 2,2-dimethylchromene (**16**). Under the conditions described above, aziridination of these alkene substrates afforded the products **17**–**19**, **5**, **20**–**26** (see Table 3) in 1–57% *ee* with substrate conversions of 41–99% (entries 1–17). The observed aziridine selectivities (that is, the chemoselectivities defined as the yields of aziridines based on the substrates consumed) range from 72–94%. We also performed the aziridination of styrene catalyzed by complex **1** under a very low catalyst loading of 0.05 mol% (**1**:PhI=NTs:styrene molar ratio = 1:2000:5000), which led to formation of aziridine **17** in 58% yield (based on the amount of starting PhI=NTs) and 42% *ee* with 1160 catalyst turnovers.

*Stoichiometric aziridination by complex **3***: The reactions of **3** with styrenes **6**–**10**, naphthalene derivative **14**, and indene (**15**) were investigated. These reactions were carried out by employing excess alkene substrates to mitigate the autodegradation of **3** in solution. The results obtained for the reactions performed in dichloromethane at 40 °C for 2 h are listed in entries 18–24 in Table 3.

Asymmetric amidation of saturated C–H bonds: *Mass balance in the amidation catalyzed by complex **2** with PhI=NTs*: A series of benzylic hydrocarbons, including ethylbenzene (**27**), 4-methoxyethylbenzene (**28**), indan (**29**), tetralin (**30**), 2-ethylnaphthalene (**31**), and 1-ethylnaphthalene (**32**), were treated with excess PhI=NTs in the presence of ≈1.3 mol% complex **2**. When the reactions were conducted in dichloromethane at 40 °C for 2 h at a **2**:substrate:PhI=NTs molar ratio of 1:75:150, the *N*-tosylamides **33**–**38** as shown in Table 4 were formed in 3–47% *ee* with substrate conversions of 14–32%. The amide selectivities in these reactions (that is, the chemoselectivities defined as the yields of amides based on the substrates consumed) range from 78 to 91%.

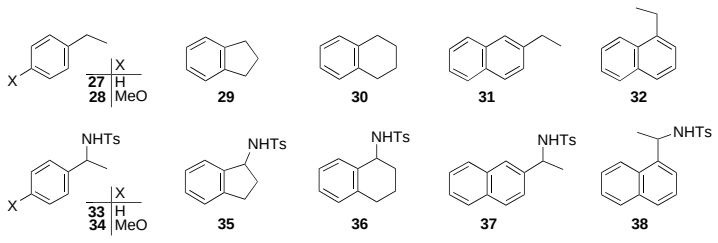
Table 3. Catalytic asymmetric PhI=NTs aziridination of aromatic alkenes by [Mn(Por*)(OH)(MeOH)] (**1**) or [Ru(Por*)(CO)(EtOH)] (**2**) and stoichiometric asymmetric aziridination of aromatic alkenes by [Ru(Por*)$(NTs)_2$] (**3**).



Entry	Substrate	Product	Catalyst	Conversion [%]	Yield [%][a]	*ee* [%][b]
catalytic aziridination[c]						
1	**6**	**17**	**1**	99	78	47
2	**6**	**17**	**2**	71	84	21
3	**7**	**18**	**1**	99	76	44
4	**7**	**18**	**2**	80	82	21
5	**8**	**19**	**1**	99	91	40
6	**8**	**19**	**2**	45	91	23
7	**9**	**5**	**1**	99	93	50
8	**9**	**5**	**2**	61	83	14
9	**10**	**20**	**1**	97	75	57
10	**10**	**20**	**2**	41	82	29
11	**11**	**21** + **22**		76	78[d]	7[e]
12	**12**	**22**	**1**	88	81	11
13	**13**	**23**	**2**	81	72	1
14	**14**	**24**	**1**	99	94	56
15	**14**	**24**	**2**	91	78	14
16	**15**	**25**	**2**	99	73	11
17	**16**	**26**	**1**	99	73	5
stoichiometric aziridination by **3**[f]						
18	**6**	**17**			78	27
19	**7**	**18**			84	29
20	**8**	**19**			90	29
21	**9**	**5**			83	28
22	**10**	**20**			61	48
23	**14**	**24**			91	43
24	**15**	**25**			72	25

[a] Yield of isolated product based on the amount of the substrate consumed (catalytic aziridination) or on the amount of complex **3** used (stoichiometric aziridination). [b] Determined by HPLC with a chiral whelk-O1 column. [c] Reaction conditions: CH_2Cl_2, 40 °C, 2 h; catalyst:substrate:(PhI=NTs) molar ratio = 1:75:150. [d] Ratio of **21**:**22** = 9:91. [e] For the *trans*-aziridine **22**. [f] Reaction conditions: CH_2Cl_2, 40 °C, 2 h.

Table 4. Asymmetric PhI=NTs amidation of benzylic hydrocarbons catalyzed by [Ru(Por*)(CO)(EtOH)] (**2**).[a]



Entry	Substrate	Product	Conversion [%]	Yield [%][b]	*ee* [%][c]
1	**27**	**33**	14	84	42
2	**28**	**34**	29	82	22
3	**29**	**35**	32	91	3
4	**30**	**36**	22	85	28
5	**31**	**37**	23	84	47
6	**32**	**38**	32	78	25

[a] Reaction conditions: CH_2Cl_2, 40 °C, 2 h; catalyst:substrate:(PhI=NTs) molar ratio = 1:75:150. [b] Yield of isolated product based on the amount of the substrate consumed. [c] Determined by HPLC with a chiral AD column.

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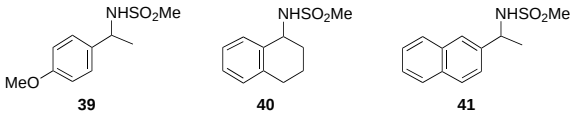
*Amidation catalyzed by complex **1** or **2** with "PhI(OAc)$_2$ + NH$_2$SO$_2$Me"*: Reaction of 4-methoxyethylbenzene (**28**), tetralin (**30**), and 2-ethylnaphthalene (**31**) with the commercially available reagents PhI(OAc)$_2$ and NH$_2$SO$_2$Me in dichloromethane containing 1 mol% complex **1** or **2** at 40 °C for 2 h produced the *N*-substituted methanesulfonamide **39**–**41** in 40–56% *ee* with amide selectivities of 84–92% (Table 5).

Table 5. Asymmetric amidation of benzylic hydrocarbons with "PhI(OAc)$_2$ + NH$_2$SO$_2$Me" catalyzed by [Mn(Por*)(OH)(MeOH)] (**1**) or [Ru(Por*)(CO)(EtOH)] (**2**).[a]



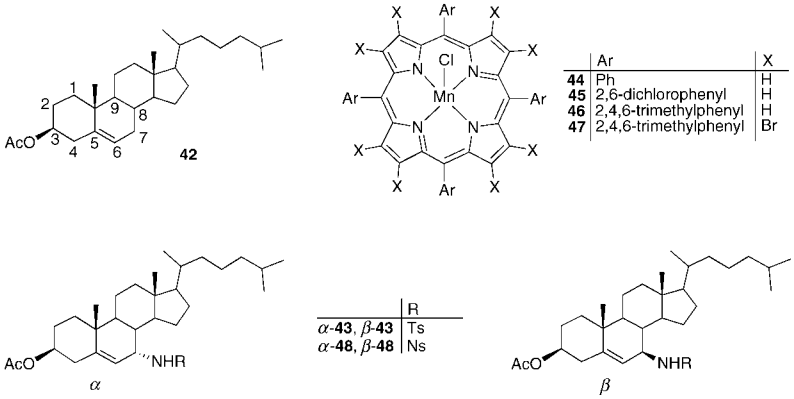
Entry	Substrate	Product	Catalyst	Conversion [%]	Yield [%][b]	*ee* [%][c]
1	**28**	**39**	**1**	26	84	50
2	**30**	**40**	**1**	22	84	46
3	**31**	**41**	**1**	21	92	56
4	**31**	**41**	**2**	34	90	40

[a] Reaction conditions: CH_2Cl_2, 40 °C, 2 h; catalyst:substrate: PhI(OAc)$_2$:NH$_2$R molar ratio = 1:100:125:150. [b] Yield of isolated product based on the amount of the substrate consumed. [c] Determined by HPLC with a chiral OD column.

*Amidation of a cholesteryl derivative catalyzed by complex **1** with PhI=NTs or "PhI(OAc)$_2$ + NH$_2$R (R = Ts, Ns)"*: The catalytic amidation of a cholesteryl derivative was explored by employing complex **1** as the catalyst. We first studied the reaction of cholesteryl acetate (**42**) with PhI=NTs in dichloromethane at 40 °C in the presence of ≈1.3 mol% complex **1**, which afforded the amide **43** as a mixture of α and β isomers with an 82% chemoselectivity (defined as the yield of **43** based on the **42** consumed), as shown in entry 1 of Table 6. The amidation is α-selective,[15] with an α:β ratio of 4.2:1. To examine the effect of porphyrin ligand on the diastereoselectivity in the amidation reactions, we treated **42** with PhI=NTs in the presence of other manganese porphyrins **44**–**47** depicted in Table 6 under the conditions identical to those employed for complex **1**. The α:β ratios observed for **44**–**47** range from 1.7:1 to 3.2:1 (entries 2–5 in Table 6), all lower than that observed for complex **1** (entry 1). Lastly, we investigated the amidation of **42** catalyzed by complex **1** with commercially available reagents PhI(OAc)$_2$ and NH$_2$R (R = Ts, Ns). These catalytic reactions were conducted in dichloromethane (entries 6 and 7 in Table 6) and in acetonitrile (entry 8 in Table 6) at a **1**:**42**:PhI(OAc)$_2$:NH$_2$R molar ratio of 1:100:125:150. The amides **43** and **48** (see Table 6) were again formed as mixtures of α and β isomers with α:β ratios of 3.6:1 (**43**), 1.8:1 (**48**, in dichloromethane), and 1.2:1 (**48**, in acetonitrile) (entries 6–8 in Table 6). The α:β ratio of 3.6:1 and the amide selectivity of 81% obtained for the "PhI(OAc)$_2$ + NH$_2$Ts" amidation of **42** are comparable to those obtained for the corresponding PhI=NTs amidation although the former amidation system gave rise to a lower substrate conversion (compare entries 1 and 6 in Table 6).

Kinetic studies of the reactions between complex 3 and hydrocarbons: We determined the second-order rate constants (k_2) for the reactions of **3** with a variety of aromatic alkenes including styrene and para-substituted styrenes 4-X–C$_6$H$_4$CH=CH$_2$ (X = H: **6**, Me: **7**, F: **49**, Cl: **9**, CF$_3$: **50**), 2-bromostyrene (**10**), 2-vinylnaphthalene (**14**), and indene

Table 6. Amidation of cholesteryl acetate (**42**) with PhI=NTs or "PhI(OAc)$_2$ + NH$_2$R (R = Ts, Ns)" catalyzed by [Mn(Por*)(OH)(MeOH)] (**1**) and other manganese porphyrins **44**–**47**.[a]



Entry	Nitrogen source	Product	Catalyst	Conversion [%]	Yield [%][b]	Ratio of α:β[c]
1	PhI=NTs	α-**43** + β-**43**	**1**	49	82	4.2:1
2	PhI=NTs	α-**43** + β-**43**	**44**	43	74	1.7:1
3	PhI=NTs	α-**43** + β-**43**	**45**	35	92	1.9:1
4	PhI=NTs	α-**43** + β-**43**	**46**	29	90	1.8:1
5	PhI=NTs	α-**43** + β-**43**	**47**	24	88	3.2:1
6	PhI(OAc)$_2$ + NH$_2$Ts	α-**43** + β-**43**	**1**	27	81	3.6:1
7	PhI(OAc)$_2$ + NH$_2$Ns	α-**48** + β-**48**	**1**	12	87	1.8:1
8[d]	PhI(OAc)$_2$ + NH$_2$Ns	α-**48** + β-**48**	**1**	21	90	1.2:1

[a] Reaction conditions: CH_2Cl_2, 40 °C, 2 h; catalyst:substrate:(PhI=NTs) molar ratio = 1:75:150; catalyst:substrate:PhI(OAc)$_2$:NH$_2$R molar ratio = 1:100:125:150. [b] Yield of isolated product based on the amount of **42** consumed. [c] Determined by ^{1}H NMR spectroscopy. [d] In MeCN.

(**15**), and benzylic hydrocarbons including ethylbenzene and *para*-substituted ethylbenzenes 4-X−$C_6H_4CH_2CH_3$ (X = H: **27**, MeO: **28**, Me: **51**, F: **52**, Cl: **53**, Br: **54**) and 2-ethylnaphthalene (**31**). The k_2 values obtained in dichloromethane containing pyrazole (2% *w*/*w*) at 298 K are compiled in Table 7. We previously reported the k_2 values for the reactions of [Ru(tpp)$(NTs)_2$] (tpp = *meso*-tetraphenylporphyrinato dianion) with some of the foregoing hydrocarbons under the same conditions;[2e] those k_2 values are also shown in Table 7 for comparison.

Table 7. Second-order rate constants (k_2) for nitrogen-atom transfer from [Ru(Por*)$(NTs)_2$] (**3**) to hydrocarbons in dichloromethane containing pyrazole (2% w/w) at 298 K. The k_2 values for nitrogen-atom transfer from [Ru(tpp)$(NTs)_2$] to the same hydrocarbons (from ref. [2e]) are also included for comparison.

Entry	Hydrocarbon	$10^3 k_2$ [dm^3 mol^{-1} s^{-1}]	
		[Ru(Por*)$(NTs)_2$] (**3**)	[Ru(tpp)$(NTs)_2$]
1	styrene (**6**)	13.7 ± 0.5	9.0 ± 0.1
2	4-methylstyrene (**7**)	35.6 ± 1.4	16.0 ± 0.8
3	4-fluorostyrene (**49**)	18.7 ± 0.5	11 ± 1
4	4-chlorostyrene (**9**)	19.9 ± 0.3	8.8 ± 0.1
5	4-trifluoromethylstyrene (**50**)	8.1 ± 0.3	3.2 ± 0.2
6	2-bromostyrene (**10**)	9.9 ± 0.5	
7	2-vinylnaphthalene (**14**)	42.5 ± 0.5	
8	indene (**15**)	40.3 ± 0.6	
9	ethylbenzene (**27**)	3.92 ± 0.06	3.60 ± 0.07
10	4-methoxyethylbenzene (**28**)	18.9 ± 0.7	16.5 ± 0.3
11	4-methylethylbenzene (**51**)	6.1 ± 0.1	6.8 ± 0.1
12	4-fluoroethylbenzene (**52**)	5.9 ± 0.4	4.3 ± 0.1
13	4-chloroethylbenzene (**53**)	3.7 ± 0.1	5.0 ± 0.1
14	4-bromoethylbenzene (**54**)	6.6 ± 0.6	
15	2-ethylnaphthalene (**31**)	21.0 ± 0.5	

Discussion

Metalloporphyrin-mediated nitrogen-atom transfer to hydrocarbons: Metal-mediated nitrogen-atom transfer to hydrocarbons constitutes an appealing route to aziridines and amides/amines. The aziridination of alkenes and amidation of saturated C−H bonds with iminoiodanes catalyzed by a metalloporphyrin were first reported by the groups of Mansuy[2b] and Breslow,[5a] respectively, in the early 1980s. Since then, a number of iminoiodane aziridinations/amidations of hydrocarbons catalyzed by iron, manganese, and ruthenium porphyrins have been studied.[2c, 5b–e] Surprisingly, the catalyst turnover numbers in these reactions are usually less than 50, not significantly higher than those observed for the nitrogen-atom transfer catalyzed by non-porphyrin metal complexes.[16] Recently, we reported the PhI=NTs aziridination/amidation of hydrocarbons catalyzed by an electron-deficient manganese porphyrin, [Mn(tpfpp)Cl] (tpfpp = *meso*-tetra(pentafluorophenyl)porphyrinato dianion), which features up to 2600 catalyst turnovers.[5f]

The chiral manganese and ruthenium porphyrins **1** and **2** are the first metalloporphyrins that have been found to be able to catalyze *asymmetric* nitrogen-atom transfer to hydrocarbon substrates. In our preliminary works on aziridinations catalyzed by complex **1**,[6] and amidations catalyzed by complex **1** or **2**,[7] only the aziridination of substrates **6**–**10** and the amidation of substrates **27**–**32** were reported, both with PhI=NTs as the nitrogen source. The reactions, except the amidation of **27**, were all conducted using *excess substrates* (≥20-fold excess for aziridination and fivefold excess for amidation), which hampered the determination of substrate conversions and aziridine or amide selectivities in the catalysis. The present work shows that, with a twofold *excess PhI=NTs*, **1**-catalyzed aziridinations of **6**–**10**, **14**, and **16**, and **2**-catalyzed aziridination of **16** resulted in substrate conversions close to 100% (see Table 3). The substrate conversions in **2**-catalyzed amidations of **27**–**32** are significantly lower (compare Table 3 and Table 4). For the hydrocarbons **6**–**16** and **27**–**32**, the aziridine or amide selectivities are good-to-excellent, with up to 57% *ee* observed for the aziridinations and up to 47% *ee* for the amidations.[17] The 1160 catalyst turnovers obtained for **1**-catalyzed aziridination of styrene is fairly high, which, to our knowledge, is the highest turnover number ever reported for a metal-complex-catalyzed *asymmetric* nitrogen-atom-transfer reaction.

The present work also reveals that complex **1** can catalyze the PhI=NTs amidation of steroid **42** in a diastereoselective manner (α:β = 4.2:1).[18] Manganese complexes **44**–**47** bearing nonchiral porphyrin ligands can catalyze the PhI=NTs amidation of **42** as well, but all afforded a lower diastereoselectivity. These manganese-porphyrin-catalyzed amidation reactions are highly regio- and chemoselective: only the amidation of the allylic C−H bonds at C-7 (see Table 6) was observed and the amide **43** was formed with up to 92% chemoselectivity.

It is remarkable that the "PhI$(OAc)_2$ + NH_2R" amidation protocol we developed previously by using nonchiral ruthenium catalysts[5f, 19] is also effective for the asymmetric amidations.[20] The amidation of 4-methoxyethylbenzene (**28**), tetralin (**30**), and 2-ethylnaphthalene (**31**) with "PhI$(OAc)_2$ + NH_2SO_2Me" catalyzed by complex **1** or **2** afforded the corresponding N-substituted methanesulfonamides **39**–**41** in 40–56% *ee* (Table 5), with substrate conversions of 21–34% comparable to those given in Table 4 for the PhI=NTs amidations. This is so far the only example of a metal-complex-catalyzed asymmetric nitrogen-atom transfer directly with "PhI$(OAc)_2$ + NH_2R" as the nitrogen source,[21] which realized an enantioselective formation of *N*-substituted methanesulfonamides from direct amidation of saturated C−H bonds catalyzed by a metal complex.

Mechanistic aspects of 2-catalyzed nitrogen-atom transfer to hydrocarbons: Despite a wide proposal of metal–imido species as the active intermediates in metal-complex-catalyzed nitrogen-atom-transfer reactions with iminoiodanes, isolation or direct observation of such intermediates remains a serious challenge in most cases. For example, no imidomanganese porphyrins have been detected in the reactions of iminoiodanes with either complex **1** or any other manganese porphyrins. The successful isolation of aziridination- and amidation-active tosylimido ruthenium porphyrin [Ru(Por*)$(NTs)_2$] (**3**) provides a useful insight into the mechanism of asymmetric nitrogen-atom-transfer reactions catalyzed by complex **2**.

From the results in Table 3, it is evident that the alkene aziridination by **3** afforded the aziridines in the yields and *ee*

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values roughly comparable to the aziridine selectivities and *ee* values observed for aziridinations catalyzed by complex **2** with PhI=NTs. A similar phenomenon was also noted for the stoichiometric amidation by **3**[7] and the PhI=NTs amidation catalyzed by **2** (Table 4). These observations, together with the facile formation of **3** from **2** and PhI=NTs, suggest the involvement of **3** as an active intermediate in the asymmetric aziridination or amidation processes catalyzed by complex **2**.

We previously isolated several aziridination- and amidation-active, *nonchiral, sterically-unencumbered* bis(tosylimido)ruthenium(VI) porphyrins and studied the mechanisms of the reactions between [Ru(tpp)(NTs)$_2$] and styrenes or benzylic hydrocarbons in considerable detail.[2e] The results in that work reveal that the aziridination of styrenes by [Ru(tpp)(NTs)$_2$] most probably occurs by the rate-limiting formation of a benzylic carboradical intermediate rather than in a concerted manner, whereas the amidation of ethylbenzenes most probably proceeds by hydrogen-atom abstraction by [Ru(tpp)(NTs)$_2$] to form benzylic radicals followed by scavenging of the radicals by the ruthenium porphyrin.

Similar mechanisms may remain valid for the reactions between the chiral imido complex **3** and styrenes or benzylic hydrocarbons considering that both **3** and [Ru(tpp)(NTs)$_2$] are bis(tosylimido)ruthenium(VI) *meso*-tetraarylporphyrins. Indeed, the aziridination by **3** also appears to occur by a nonconcerted pathway: the aziridination of *cis*-β-methylstyrene **11** catalyzed by complex **2** afforded a mixture of cis and trans aziridines **21** and **22** (entry 11 in Table 3), like the aziridination of the same alkene by [Ru(tpp)(NTs)$_2$]. Moreover, the substituent effects in **3**- and [Ru(tpp)(NTs)$_2$]-mediated aziridinations/amidations are similar. As shown in Table 7, for both of the imido complexes, the aziridination of para-substituted styrenes is basically promoted by electron-donating substituents but retarded by electron-withdrawing substituents, whereas the amidation of para-substituted ethylbenzenes is basically promoted by either electron-donating or -withdrawing substituents. Further, the larger k_2 values observed for 2-vinyl- and 2-ethylnaphthalene than for styrenes and ethylbenzenes, respectively (see Table 7), are consistent with the intermediacy of benzylic radicals in the reactions in view of a wider conjugation in the radicals with a naphthyl ring than with a phenyl ring.

However, we noted the following significant differences between the nitrogen-atom-transfer reactions mediated by **3** and [Ru(tpp)(NTs)$_2$]. First, the ratio of *cis*- versus *trans*-aziridine (**21**:**22**) in the aziridination of **11** catalyzed by **2** (9:91) is substantially lower than that mediated by [Ru(tpp)(NTs)$_2$] (34:66).[2e] Second, the aziridination of styrenes mediated by **3** is considerably faster than that by [Ru(tpp)(NTs)$_2$] (as reflected by the k_2 values compiled in Table 7). Third, the log k_R versus (σ_{mb}, σ_{JJ}·) plot[22] for **3**-mediated aziridination of **6** and *para*-substituted styrenes **7**, **9**, **49**, and **50** features ρ_{mb} of -0.58 and ρ_{JJ}· of 1.05 with $|\rho_{mb}/\rho_{JJ}$·$|$ of 0.55, in contrast to the ρ_{mb} of -1.05 and ρ_{JJ}· of 0.52 with $|\rho_{mb}/\rho_{JJ}$·$|$ of 2.02 observed for [Ru(tpp)(NTs)$_2$]-mediated aziridination of the same alkenes.[2e] Fourth, for the **3**-mediated amidation of ethylbenzenes **27**, **28**, and **51**–**53**, plotting log k_R against the radical parameter TE[23] did not give a good linearity,[24] unlike the case of complex [Ru(tpp)(NTs)$_2$].[2e]

The above differences between the nitrogen-atom-transfer reactions of **3** and [Ru(tpp)(NTs)$_2$] should stem from the different electronic or steric properties of the porphyrin ligands. Fusing two electron-donating, bulky norbornane moieties to each of the four *meso*-phenyl groups of tpp to form Por* would render the macrocycle more electron-rich and sterically more demanding. This would make the *N*-tosylimido groups in **3** less electrophilic than those of [Ru(tpp)(NTs)$_2$] and would provoke a larger steric interaction between **3** and hydrocarbons, both are expected to make **3** react more slowly with styrenes than [Ru(tpp)(NTs)$_2$] (note the electrophilic nature of the attack of styrenes by **3** and [Ru(tpp)(NTs)$_2$] as reflected by the *negative* ρ_{mb} values described above). In this context, the larger aziridination rates observed for **3** than for [Ru(tpp)(NTs)$_2$] are striking, which might be associated with the different steric interaction between the tosylimido groups and the porphyrin ligands in **3** and [Ru(tpp)(NTs)$_2$].

The tosylimido groups in **3** and [Ru(tpp)(NTs)$_2$] are expected to have essentially linear Ru-N-Ts moieties, a geometry previously observed for the same imido groups in the X-ray crystal structures of bis(tosylimido)osmium(VI) porphyrins.[3q, 25] Suppose that the TsN=Ru=NTs moieties of **3** and [Ru(tpp)(NTs)$_2$] have the same metrical parameters as the TsN=Os=NTs moieties of bis(tosylimido)osmium(VI) porphyrins,[26] modeling studies reveal that the rotation of the Ts groups in **3** about the N–S bonds is hampered by the steric interaction between the Ts groups and the norbornane moieties of the Por* ligand (see Figure 2a). However, the Ts groups in [Ru(tpp)(NTs)$_2$] can freely rotate about the N–S bonds (see Figure 2b). The rapid rotation of Ts groups about the S–N bond in [Ru(tpp)(NTs)$_2$] could make it harder for styrenes to approach the tosylimido N atoms (compare Figure 2c and Figure 2d) and thus slow down the nitrogen-atom-transfer reactions. This may rationalize the faster reactions of **3** with styrenes. Alternatively, if complex **3** favors a structure that has a smaller steric interaction between the Ts groups and the norbornane moieties (relative to the structure shown in Figure 2a), the Ru=NTs bonds in the complex should be longer than those in [Ru(tpp)(NTs)$_2$]. This would make **3** have weaker Ru=NTs bonds, which may also account for its faster reactions with styrenes.[27]

Concerning the modes by which terminal aromatic alkenes ArCH=CH$_2$ (such as styrenes and 2-vinylnaphthalene) approach the tosylimido N atoms of **3** or [Ru(tpp)(NTs)$_2$], several possibilities as shown in Scheme 3 are to be considered. Evidently, the linear Ru–N–Ts arrangements would prevent the alkenes from approaching the tosylimido N atoms in a "top-on" manner (Scheme 3a). "Side-on" approaches as shown in Scheme 3b and Scheme 3c are possible, which minimize the interaction of the Ar groups with the porphyrin ligands and allow a concerted nitrogen-atom transfer via transition states **55** and **56** (see the inset to Scheme 3). The transition state **56** may be more stable than **55** since the former has a larger separation between the Ar and Ts groups. However, even in **56**, the steric interaction between the Ar and Ts groups could still be significant due to their mutually

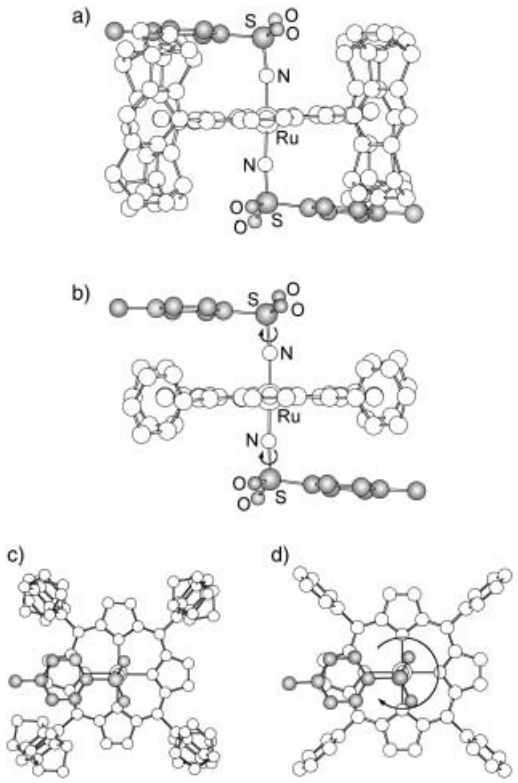
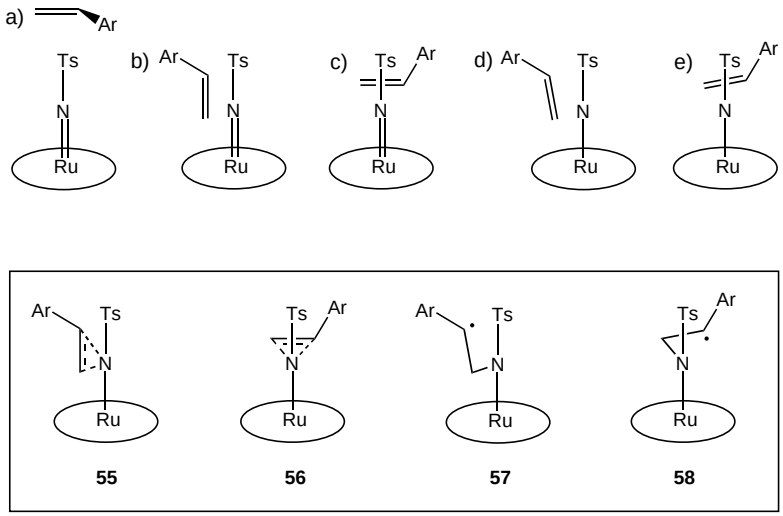


Figure 2. Side-view model structures of a) [Ru(Por*)(NTs)$_2$] (**3**) and b) [Ru(tpp)(NTs)$_2$]. The top-views of these model structures are depicted in c) and d), respectively. Hydrogen atoms are not shown and the atoms of the Ts groups are filled with grey colors. The modeling was based on the X-ray crystal structures of complex **4** reported here and complex [Os(tpp)(NTs)$_2$] reported in reference [25].



Scheme 3. a) Top-on and b)–e) side-on approaches of terminal aromatic alkenes to the N atoms of the tosylimido groups in **3** or [Ru(tpp)(NTs)$_2$] (only one tosylimido axial group is shown in each case). The inset shows the transition states **55**–**58** corresponding to the side-on approaches in b)–e), respectively.

cis arrangement in the preformed aziridine. In fact, all the X-ray crystal structures of monocyclic C-substituted *N*-tosylaziridines feature a *trans* rather than *cis* configuration[13g] (note also the trans configuration of aziridine **5** in the structure of **4**). Therefore, the alkenes may preferentially approach the tosylimido N atoms in a manner as shown in Scheme 3d or Scheme 3e, which results in a nonconcerted nitrogen-atom transfer via benzylic radical intermediates **57** or **58** to mitigate the steric interaction between the Ar and Ts groups. In our previous kinetic studies on the aziridinations by [Ru(tpp)(NTs)$_2$],[2e] a concerted nitrogen-atom-transfer pathway is also disfavored. The formation of the O-bound aziridine adduct **4**, rather than an N-bound aziridine adduct similar to transition state **55** or **56**,[28] from reaction of **2** with **5** provides additional evidence in disfavor of the concerted pathway in the ruthenium porphyrin-mediated aziridinations.

Conclusion

We have shown that the nitrogen-atom-transfer reactions between PhI=NTs and a variety of hydrocarbons catalyzed by chiral metalloporphyrins [Mn(Por*)(OH)(MeOH)] (**1**) and [Ru(Por*)(CO)(EtOH)] (**2**) feature good-to-excellent aziridine selectivities for aromatic alkenes and good-to-excellent amide selectivities for benzylic hydrocarbons. Reaction of cholesteryl acetate with PhI=NTs in the presence of catalyst **1** afforded the corresponding amide in high regio- and chemoselectivity and moderate diastereoselectivity. The isolation of the aziridination- and amidation-active chiral imido ruthenium porphyrin [Ru(Por*)(NTs)$_2$] (**3**) and the ruthenium porphyrin aziridine adduct [Ru(Por*)(CO)(TsAz)] (**4**, TsAz = *N*-tosyl-2-(4-chlorophenyl)aziridine) with an O- rather than N-bound aziridine ligand provides useful insight into the mechanism of asymmetric nitrogen-atom-transfer reactions catalyzed by complex **2**. Kinetic studies of the reactions between **3** and aromatic hydrocarbons disclose a significant effect of porphyrin ligand on the nitrogen-atom-transfer reactions of bis(tosylimido)ruthenium(VI) porphyrins. Finally, the present work first demonstrated the feasibility of using "PhI(OAc)$_2$ + NH$_2$R" as the nitrogen source in metal-catalyzed asymmetric nitrogen-atom-transfer reactions, and by employing this amidation protocol, N-substituted methanesulfonamides became accessible in up to 56% *ee* from direct amidation of saturated C–H bonds catalyzed by complex **1** or **2**.

Experimental Section

General: PhI(OAc)$_2$ (Aldrich), NH$_2$Ts (Aldrich), NH$_2$Ns (Acros), NH$_2$SO$_2$Me (Aldrich), cholesteryl acetate (Acros), and all the solvents (AR grade), except dichloromethane, were used as received. Dichloromethane and aromatic hydrocarbons were purified as described elsewhere.[2e] H$_2$(Por*),[1g, 9] PhI=NTs,[29] *cis*-β-methylstyrene,[30] and complexes **1**,[6] **2**,[3k] **44**–**47**[31] were prepared according to the literature methods. ^{1}H NMR spectra were measured on a Bruker DPX300 spectrometer with CDCl$_3$ as the solvent (the chemical shifts are relative to tetramethylsilane). IR spectra were recorded on a Bio-Rad FT-IR spectrometer (KBr pellet). UV/Vis spectra were obtained on a HP8453 diode array spectrophotometer. Mass spectra were measured on a Finnigan

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MAT 95 mass spectrometer. HPLC measurements were carried out on a HP 1050 Series HPLC. Elemental analyses were performed by the Institute of Chemistry, the Chinese Academy of Sciences.

Synthesis of bis(tosylimido)ruthenium(VI) porphyrin [Ru(Por*)(NTs)$_2$] (3): A mixture of [Ru(Por*)(CO)(EtOH)] (**2**, 0.05 mmol) and PhI=NTs (0.2 mmol) in dichloromethane (10 mL) was stirred at room temperature under argon for 5 min. The mixture was then evaporated to dryness in vacuo followed by chromatography on a short column of neutral alumina with dichloromethane as the eluent. The first red band was collected and the solvent was removed in vacuo, affording complex **3** as a dark purple powder in 64 % yield. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 8.77$ (s, 8H), 7.38 (s, 4H), 6.19 (d, $J = 8.2$ Hz, 4H), 4.90 (d, $J = 8.1$ Hz, 4H), 3.57 (s, 8H), 2.72 (s, 8H), 1.98 (m, 8H), 1.87 (m, 14H), 1.36 (m, 24H), 1.11 (m, 8H); IR (KBr): $\tilde{\nu} = 1019$ cm^{-1} ("oxidation-state marker" band); UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 424 (5.26), 536 (4.14), 570 nm (3.76, sh); elemental analysis calcd (%) for $C_{98}H_{90}N_6O_4S_2Ru \cdot 2CH_2Cl_2$ (1750.87): C 68.60, H 5.41, N 4.80; found: C 69.04, H 5.40, N 4.29.

Synthesis of [Ru^{II}(Por*)(CO)(TsAz)] (4): To a solution of [Ru^{II}(Por*)-(CO)(EtOH)] (10 mg, 7.6 μmol) in chloroform (2 mL) was added free aziridine **5** (9.4 mg, 30 μmol). The mixture was stirred for 1 h, and then treated with excess hexane, leading to the formation of a dark purple precipitate. The precipitate was collected by filtration, washed with hexane, and air-dried. Yield: 85 %; ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 8.55$ (dd, 8H), 7.37 (s, 4H), 3.56 (m, 8H), 2.72 (s, 8H), 1.97 (m, 8H), 1.89 (m, 8H), 1.39–0.86 (m, 32H), TsAz: 7.80 (d, $J = 8.3$ Hz, 4H), 7.36 (d, 4H, partially overlapped with δ 7.37 signal), 7.28 (d, $J = 8.6$ Hz, 4H), 7.16 (d, $J = 8.4$ Hz, 4H), 3.67 (m, 1H), 2.91 (d, $J = 7.2$ Hz, 1H), 2.35 (d, $J = 4.4$ Hz, 1H), 2.43 (s, 3H); IR (KBr): $\tilde{\nu} = 1935$ cm^{-1} (CO); UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 414 (5.02), 529 nm (4.05); elemental analysis calcd (%) for $C_{100}H_{90}ClN_5O_3SRu \cdot 5/4\,CHCl_3$ (1727.63): C 70.39, H 5.32, N 4.05; found: C 70.55, H 5.61, N 3.83.

General procedure for asymmetric aziridination/amidation with PhI=NTs catalyzed by complex 1 or 2: A solution of substrate (0.15 mmol) in dry dichloromethane (4 mL) was added by syringe into a Schlenk flask containing **1** or **2** (0.002 mmol) and molecular sieves (4 Å, 50 mg). The mixture was stirred at room temperature for 10 min, then treated with PhI=NTs (0.30 mmol), and maintained at 40 °C for 2 h. After the mixture was cooled to room temperature, the molecular sieves were filtered off and washed with dichloromethane. The filtrate and washings were combined and then evaporated to dryness. The product was purified by column chromatography on silica gel with *n*-hexane/ethyl acetate (6:1 v/v) as the eluent.

α-**43**: The spectral data of this compound are identical with those reported in the literature.[15]

β-**43**: ^{1}H NMR ($CDCl_3$): $\delta = 7.73$ (d, $J = 8.2$ Hz, 2H), 7.30 (d, $J = 8.2$ Hz, 2H), 4.76 (s, 1H), 4.51 (m, 1H), 4.04 (d, $J = 9.2$ Hz, 1H), 3.65 (t, 1H), 2.44 (s, 3H), 2.00 (s, 3H), 2.20–0.85 (m, 41H); MS: m/z: 597 $[M]^+$.

General procedure for asymmetric amidation with "PhI(OAc)$_2$ + NH$_2$R (R = Ts, Ns, SO$_2$Me)" catalyzed by complex 1 or 2: To a well-stirred suspension of molecular sieves (4 Å, 50 mg) in dry dichloromethane (4 mL) containing **1** or **2** (0.002 mmol) at room temperature was added the substrate (0.20 mmol) by means of a syringe. After 10 min, NH_2R (0.30 mmol) and $PhI(OAc)_2$ (0.25 mmol) were added and the mixture was stirred at 40 °C for 2 h. The solution was then filtered and the products were purified by column chromatography on silica gel with *n*-hexane/ethyl acetate (6:1 v/v) as the eluent.

39: ^{1}H NMR ($CDCl_3$): $\delta = 7.26$ (d, $J = 8.4$ Hz, 2H), 6.90 (d, $J = 8.3$ Hz, 2H), 4.62 (m, 1H), 4.55 (d, $J = 6.0$ Hz, 1H), 3.81 (s, 3H), 2.62 (s, 3H), 1.52 (d, $J = 6.9$ Hz, 3H); MS: m/z: 229 $[M]^+$; HRMS m/z $[M]^+$ calcd for $C_{10}H_{15}NO_3S$: 229.0773, found: 229.0769.

40: ^{1}H NMR ($CDCl_3$): $\delta = 7.42$ (m, 1H), 7.20 (m, 2H), 7.09 (m, 1H), 4.65 (m, 1H), 4.51 (d, $J = 7.9$ Hz, 1H), 3.07 (s, 3H), 2.80 (m, 2H), 2.10 (m, 2H), 1.89 (m, 2H); MS: m/z: 225 $[M]^+$; HRMS m/z $[M]^+$ calcd for $C_{11}H_{15}NO_2S$: 225.0824, found: 225.0837.

41: M.p. 148–149 °C; ^{1}H NMR ($CDCl_3$): $\delta = 7.83$ (m, 4H), 7.49 (m, 3H), 4.85 (m, 1H), 4.75 (d, $J = 5.9$ Hz, 1H), 2.62 (s, 3H), 1.63 (d, $J = 6.9$ Hz, 3H); MS: m/z: 249 $[M]^+$; HRMS m/z $[M]^+$ calcd for $C_{13}H_{15}NO_2S$: 249.0824, found: 249.0819.

α- and β-**48**: ^{1}H NMR ($CDCl_3$): $\delta = 8.37$ (m, 2H), 8.05 (m, 2H), 5.63 (d, $J = 5.7$ Hz, 1H), 5.23 (s, 1H), 4.55 (m, 1H), 3.83 (m, 1H), 3.64 (m, 1H), 2.04 (s, 3H), 2.22–0.71 (m, 41H); MS: m/z: 628 $[M]^+$.

General procedure for the stoichiometric asymmetric aziridination/amidation by complex 3: Complex **3** (0.05 mmol) was added to a solution of substrate (2 mmol) in dichloromethane (4 mL) containing pyrazole (2 % w/w) in a 10-mL Schlenk tube. The mixture was stirred for 2 h at 40 °C. After removal of solvent, the amidation products were purified by column chromatography on silica gel with *n*-hexane/ethyl acetate (6:1 v/v) as the eluent.

Kinetic studies: Kinetic measurements were performed on a HP 8453 Diode Array spectrophotometer with an IBM-compatible PC and equipped with a Lauda RM 6 circulating water bath by using standard 1.0-cm quartz cuvettes. The temperature of solutions during kinetic experiments was maintained to within ±0.2 °C. The rates of nitrogen-atom transfer from **3** to hydrocarbon substrates were measured by monitoring the decrease in absorbance of **3** at 424 nm in dichloromethane containing pyrazole (2 % w/w) with a [substrate]:[**3**] concentration ratio of ≥100:1, a condition identical to that employed in the rate measurements for the reactions between [Ru(tpp)(NTs)$_2$] and hydrocarbons.[2e] Pseudo-first-order rate constants (k_{obs}) were determined from the ($A_f - A_t$) versus t plot (A_f: the final absorbance, A_t: the absorbance at time t) by nonlinear least-squares fits of the data over four half-lives ($t_{1/2}$) according to Equation (1), where A_i is the initial absorbance.

$$(A_f - A_t) = (A_f - A_i)\exp(-k_{obs}t) \quad (1)$$

Second-order rate constants, k_2, were obtained from the plots of k_{obs} versus substrate concentration by linear least-squares fitting. For each substrate, at least four data points were used to determine the k_2 value, with the straight line fit giving an R value of >0.99. The errors in the k_2 values shown in Table 7 are the errors of the straight-line fits.

X-ray structure determination of complex 4: Single crystals of **4** were obtained by slow diffusion of hexane into a solution of **4** in chloroform containing free aziridine **5**. A crystal of dimensions 0.5 × 0.2 × 0.15 mm mounted in a glass capillary was used for data collection at 28 °C on a MAR diffractometer with a 300 mm image plate detector using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The images were interpreted and the intensities integrated by using program DENZO. The structure was solved by direct methods by employing the SHELXS-97 program. Many non-hydrogen atoms including the ruthenium atom were located by direct methods. The positions of the other non-hydrogen atoms were found after successful refinement (against F^2) by full-matrix least-squares using SHELXL-97. In the final stage of the least-squares refinement, all non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were generated by SHELXL-97. The positions of hydrogen atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated carbon atoms.

CCDC-172416 (**4**) contains the supplementary crystallographic data (excluding structure factors) for the structure reported in this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

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[27] The larger k_2 values for the amidation of ethylbenzenes **27**, **28**, and **52** by **3** than by [Ru(tpp)$(NTs)_2$] (see Table 7) may be rationalized in a similar manner. However, it is unclear why the amidations of **51** and **53** by **3** are slower than by [Ru(tpp)$(NTs)_2$].

[28] This is in contrast to the isolation of a styrene oxide adduct, [Ru(tdcpp)(CO)(styrene oxide)] (tdcpp = *meso*-tetrakis(2,6-dichlorophenyl)porphyrinato dianion), from reaction of [Ru(tdcpp)(CO)(MeOH)] with styrene oxide by Groves and co-workers. See: J. T. Groves, Y. Han, D. V. Engen, *J. Chem. Soc. Chem. Commun.* **1990**, 436.

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