0.6305. CCDC-185204 contains the supplementary crystallographic data for 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) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Highly Diastereo- and Enantioselective Intramolecular Amidation of Saturated C–H Bonds Catalyzed by Ruthenium Porphyrins**

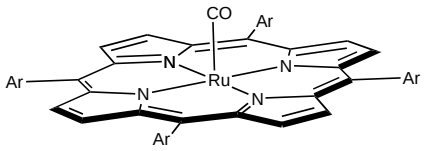
Jiang-Lin Liang, Shi-Xue Yuan, Jie-Sheng Huang, Wing-Yiu Yu, and Chi-Ming Che*

Metal-complex-catalyzed amidation of saturated C–H bonds[1–7] is increasingly attractive as a C–N bond-formation methodology. The nitrogen sources in most of these amidation reactions are iminoiodanes PhI=NR, which are prepared from $PhI(OAc)_2$ and RNH_2 and are currently accessible for rather limited types of R groups (usually $R = ArSO_2$). In very few cases can the PhI=NR amidation procedure be applied to intramolecular amidation.[1b,3c,5] About two years ago,[4d] we found that $PhI(OAc)_2$ and RNH_2 ($R = p\text{-}MeC_6H_4SO_2$, $p\text{-}NO_2C_6H_4SO_2$) could be used directly as the nitrogen source in intermolecular amidation processes. More interestingly, the "$PhI(OAc)_2$+RNH_2" amidation protocol is extendable to "$PhI(OAc)_2$+$MeSO_2NH_2$"[4d,e,g] and "$PhI(OAc)_2$+CF_3CONH_2[4d] or $PhCONH_2$[4e]", in which cases the respective iminoiodanes are explosive or unknown. We envisioned that such a "$PhI(OAc)_2$+RNH_2" amidation procedure might be applicable to a wide variety of RNH_2 compounds and could be more readily extended to intramolecular amidation, as shown in Equation (1).

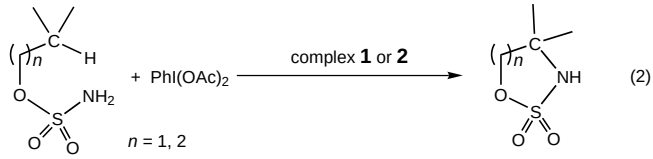
(1)

Recent work by Du Bois and co-workers[7] excellently demonstrated that reactions of a series of carbamates ($-OCONH_2$)[7a] and sulfamate esters ($-OSO_2NH_2$)[7b] with $PhI(OAc)_2$, catalyzed by dirhodium complexes, afford oxazolidinones and cyclic sulfamidates, respectively, with high regioselectivity and good to excellent diastereoselectivity. These reactions occur by the direct intramolecular amidation of saturated C–H bonds. Du Bois and co-workers found that these intramolecular amidation reactions are stereospecific, allowing synthesis of enantiomerically pure amidation products from enantiomerically pure carbamates or sulfamate esters.[7] However, it remains a challenge to realize asymmetric intramolecular amidation of saturated C–H bonds from prochiral RNH_2 substrates.

Herein, we report the first metalloporphyrin-catalyzed intramolecular amidation reactions of saturated C–H bonds that employ a "$PhI(OAc)_2$+RNH_2" procedure. The catalysts used are mainly the electron-deficient ruthenium porphyrin [Ru(tpfpp)(CO)][8] (**1**, H_2tpfpp = *meso*-tetra(pentafluorophenyl)porphyrin) and the chiral ruthenium porphyrin [Ru(por*)(CO)][9] (**2**, H_2por* = 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[10]). In the presence of these catalysts, reactions of sulfamate esters with $PhI(OAc)_2$ afforded cyclic sulfamidates with high regioselectivity and virtually complete diastereoselectivity [Equation (2)]. Remarkably, the intramolecular amidation of prochiral sulfamate esters catalyzed by **2** produced optically active cyclic sulfamidates in up to 87% *ee*.[11] This value contrasts with the highest *ee* value of



1 **2**



(2)

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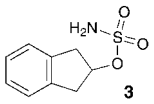
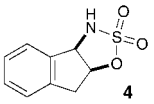
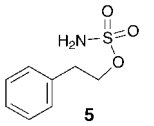
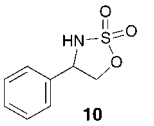
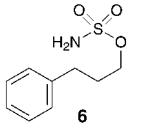
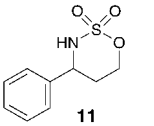
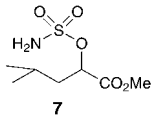
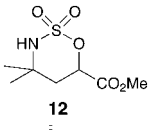
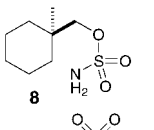
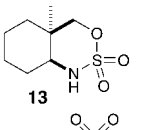
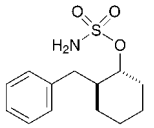
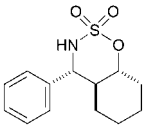
58% in the intermolecular amidation of saturated C–H bonds catalyzed by the same ruthenium porphyrin.[4c,g] Prior to this work, only in a single case did metal-complex-catalyzed intramolecular amidation of saturated C–H bonds proceed in asymmetric manner; this procedure employs the PhI=NR protocol and a chiral dirhodium catalyst and affords a cyclic sulfonamide in 10% *ee*.[3c]

The intramolecular amidation catalyzed by **1** was initially explored with sulfamate indan-2-yl ester (**3**, see Table 1) as the substrate. Treatment of **3** with 2 equiv of $PhI(OAc)_2$ in dichloromethane at 40°C, in the presence of 1.5 mol% of **1**, afforded the corresponding cyclic sulfamidate **4** in 52% yield

Table 1. Intramolecular amidation of sulfamate esters catalyzed by [Ru(tpfpp)(CO)] (**1**).[a]

Entry	Substrate	Product	Yield [%][b]
1[c]	 **3**	 **4**	52
2			61
3	 **5**	 **10**	56
4	 **6**	 **11**	77
5	 **7**	 **12**	76
6	 **8**	 **13**	88
7	 **9**	 **14**	88

[a] Reaction conditions: CH_2Cl_2, 40°C, 2 h; **1**:substrate:$PhI(OAc)_2$:Al_2O_3 0.015:1:2:2.5. [b] Yield of isolated product, based on starting substrate. [c] In the absence of Al_2O_3.

within 2 h (entry 1, Table 1). Addition of inorganic bases such as MgO and ZnO (2.5 equiv) to the amidation system increased the yield of **4** to 58%. However, organic bases (such as pyridine) and more strongly basic inorganic additives (such as K_2CO_3 and NaOH) exhibited deleterious effects. The best additive we found is Al_2O_3, which enabled us to isolate **4** in a 61% yield (entry 2, Table 1), similar to the 60% yield obtained by employing dirhodium catalyst.[7b] Examination of solvent effects revealed that dichloromethane is superior to 1,2-dichloroethane, acetonitrile, and benzene. For example, when the reaction was conducted in the latter three solvents with MgO as an additive, the yield of **4** dropped to 28, 8.3, and 45%, respectively.

Note that the reaction of **3** with $PhI(OAc)_2$ to form **4** can also be catalyzed by other achiral metalloporphyrins such as [M(tpp)Cl] (M = Fe, Mn; H_2tpp = *meso*-tetraphenylporphyrin) and [Ru(tpp)(CO)]. However, the yields of the cyclic sulfamidate obtained by employing these metalloporphyrin catalysts (15–25%, reaction conditions: dichloromethane, 40°C, MgO, 2.0 mol% catalyst) were substantially lower than those obtained by employing catalyst **1**. Non-porphyrin ruthenium complexes such as $[Ru(Me_3tacn)(CF_3CO_2)_3\cdot H_2O]$ (Me_3tacn = *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane), *trans*-$[Ru(pybox\text{-}ip)Cl_2(CH_2{=}CH_2)]$ (pybox-ip = bis(2-oxazolin-2-yl) pyridine), and $[Ru(Br_4salen)(PPh_3)_2]$ (H_2Br_4salen = 1,2-bis(3,5-dibromo-2-hydroxybenzylideneamino)cyclohexane) were ineffective or poor catalysts for this intramolecular amidation reaction, affording **4** in < 16% yields under similar conditions.

We then treated sulfamate esters **5–9** (see Table 1) with $PhI(OAc)_2$ in dichloromethane at 40°C, in the presence of catalyst **1** (1.5 mol%) and Al_2O_3, with the same substrate:-$PhI(OAc)_2$:Al_2O_3 molar ratio as for **3**. These reactions afforded cyclic sulfamidates **10–14** in 56–88% yields (entries 3–7 in Table 1). The regioselectivity of the **1**-catalyzed intramolecular amidation of **3** and **5–9** is comparable to that of the dirhodium-catalyzed analogues.[7b] For substrates **3** and **5**, only their β-C–H bonds were amidated, producing five-membered cyclic sulfamidates **4** and **10** (entries 1–3 in Table 1). For the other substrates, the amidation occurred at the secondary or tertiary γ-C–H bonds to form six-membered cyclic sulfamidates **11–14** (entries 4–7 in Table 1), although these substrates, except **8**, also contain β-C–H bonds. The yields of the six-membered cyclic sulfamidates **11–14** were substantially higher than those of the five-membered sulfamidates **4** and **10**.

Complex **1** is the most robust catalyst ever reported for the intramolecular amidation of saturated C–H bonds. The intramolecular amidation of **3** and **5–9** catalyzed by 1.5 mol% of **1** features up to 59 catalytic turnovers. By lowering the loading of **1** to 0.1 mol%, over 300 catalytic turnovers were obtained for the intramolecular amidation of **8** to form **13**. In contrast, previously reported intramolecular amidations of saturated C–H bonds all feature < 50 catalytic turnovers.[1b,3c,5,7]

Strikingly, although the intramolecular amidation of **3**, **8**, and **9** might form **4**, **13**, and **14**, respectively, as a mixture of two diastereomers, only the indicated *cis* diastereomers of **4** and **13** and the diastereomer of **14** (entry 7, Table 1) were isolated by employing catalyst **1** [12] (the other diastereomers of **4**, **13**, and **14** were not detected by ^{1}H NMR spectroscopy in the unpurified reaction mixtures). This result differs from the amidation of **8** catalyzed by a dirhodium complex,[7b] which afforded **13** as a mixture of *cis* and *trans* diastereomers in 8:1 ratio.

Excellent diastereoselectivity was also observed in the intramolecular amidation of **3** catalyzed by **2**. Treatment of **3** with $PhI(OAc)_2$ in dichloromethane at 40°C, in the presence of Al_2O_3 and 10 mol% of **2** with a substrate:$PhI(OAc)_2$:Al_2O_3 molar ratio of 1:1.4:2.5, afforded the *cis* diastereomer of **4** in 57% yield (entry 1, Table 2). The chiral auxiliaries in **2**

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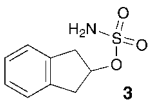
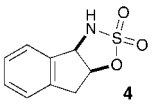
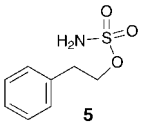
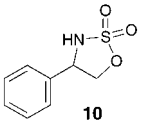
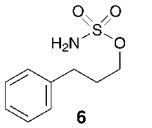
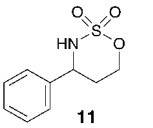
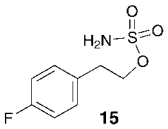
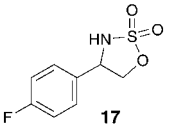
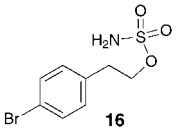
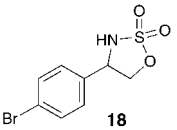
induced significant enantioselectivity in the intramolecular amidation process, with the optically active compound **4** obtained in 71% *ee* (entry 1, Table 2).

Surprisingly, when the amidation of **3** catalyzed by **2** was carried out in benzene at 80°C, the enantioselectivity observed for **4** was considerably higher (81% *ee*, entry 2, Table 2).[13] Lowering the reaction temperature to 5°C further increased the *ee* value to 82% (entry 3, Table 2); but the *ee* value decreased to 77% when the reaction was conducted in toluene at 0°C (entry 4, Table 2). The absolute configuration of the predominant enantiomer of **4** is (1*R*, 2*S*) in all cases, as determined by X-ray crystallographic studies.[14]

We also performed the **2**-catalyzed amidation of **5** and **6** under conditions similar to those for **3** (entries 5–10 in Table 2); in these cases, substantially higher *ee* values were again attained in benzene than in dichloromethane, although the yields of the cyclic sulfamidates were lower in the former solvent. The amidation of **5** in benzene at 5°C gave the highest enantiocontrol, giving optically active **10** in 87% *ee* (entry 7, Table 2). To examine the effect of *para* substituents on the asymmetric amidation of **5**, we prepared sulfamate esters **15** and **16** (see Table 2). The enantioselectivity observed in benzene for the two substrates (entries 11–14 in Table 2) was slightly lower than that for **5**.

Table 2. Asymmetric intramolecular amidation of sulfamate esters catalyzed by [Ru(por*)(CO)] (**2**).[a]

Entry	Substrate	Product	Yield [%][b]	*ee* [%][c]
1[d]	 **3**	 **4**	57	71
2			53	81
3[e]			39	82
4[f]			39	77
5[d]	 **5**	 **10**	53	69
6			43	82
7[e]			35	87
8[d]	 **6**	 **11**	77	46
9			63	79
10[e]			48	84
11	 **15**	 **17**	40	80
12[e]			20	83
13	 **16**	 **18**	46	78
14[e]			31	86

[a] Reaction conditions: C_6H_6, 80°C, 2 h; **2**:substrate:PhI(OAc)$_2$:Al_2O_3 0.1:1:1.4:2.5. [b] Yield of isolated product, based on starting substrate. [c] Determined by HPLC using a chiral OD column. [d] In CH_2Cl_2 at 40°C. [e] Reaction temperature: 5°C. [f] In toluene at 0°C.

Attempts were made to identify the intermediates in the foregoing intramolecular amidation of sulfamate esters catalyzed by ruthenium porphyrins. Treatment of **3** with PhI(OAc)$_2$ afforded a light-yellow solid,[15] which we tentatively assigned as the iminoiodane PhI=NSO$_2$(O-indan-2-yl) (**19**) by ^{1}H NMR spectroscopy.[16] Interestingly, reaction of **19** with **2** (molar ratio: 2.5:1) in dichloromethane at 40°C for 2 h produced the *cis* diastereomer of **4** in 57% yield and 85% *ee*. These values are comparable with those observed in the corresponding catalytic reaction (entry 1, Table 2).[17] In view of this observation, together with the facile formation of bis(tosylimido)ruthenium(VI) porphyrins [Ru(por)(NSO$_2$-*p*-C$_6$H$_4$Me)$_2$] from [Ru(por)(CO)] and PhI=NSO$_2$-*p*-C$_6$H$_4$Me,[4b,c,g] we propose that the bis(imido) species [Ru(por)(NSO$_2$(OR))$_2$] (por = tpfpp or por*) could be involved in the intramolecular amidation of sulfamate esters with PhI(OAc)$_2$, catalyzed by **1** or **2**. Efforts are underway to detect and isolate these intriguing species.

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[12] The structures of racemic **4**, **13**, and **14** have been determined by X-ray crystallography. CCDC-184691 (**4**), CCDC-184693 (**13**), and CCDC-184694 (**14**) contain the supplementary crystallographic data for 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 CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[13] For examples of other metal-catalyzed asymmetric reactions that show strong solvent effects on enantioselectivity, see: a) Y. Sato, N. Saito, M. Mori, *J. Am. Chem. Soc.* **2000**, *122*, 2371; b) M. Ogasawara, H. Ikeda, T. Nagano, T. Hayashi, *J. Am. Chem. Soc.* **2001**, *123*, 2089.

[14] CCDC-184692 ((1*R*,2*S*)-**4**) contains the supplementary crystallographic data for this paper.[12] The single crystal used for the structure determination was obtained from an optically active sample of **4** with 82% *ee*. The small absolute structure parameter of 0.15(12) derived from the structure determination confirms the chirality of the crystal.

[15] Following the procedures reported by Dauban and Dodd for preparation of iminoiodane $PhI{=}NSO_2(CH_2)_2SiMe_3$ from $PhI(OAc)_2$ and $Me_3Si(CH_2)_2SO_2NH_2$ (P. Dauban, R. H. Dodd, *J. Org. Chem.* **1999**, *64*, 5304).

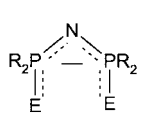
[16] ^{1}H NMR ($CDCl_3$, 400 MHz) of **19**: $\delta = 7.89$ (d, $J = 7.8$ Hz, 2H), 7.54 (t, $J = 7.4$ Hz, 1H), 7.33 (t, $J = 7.7$ Hz, 2H), 7.16 (m, 4H), 5.19 (m, 1H), 3.06 (m, 4H). The rather high instability of **19** renders it difficult to characterize this compound fully.

[17] The lower *ee* value in the catalytic reaction than in the reaction between **2** and **19** may arise from a lower loading of **2** in the former case. We once observed that reducing the loading of **2** from 10 to 2 mol% in the amidation of **6** in CH_2Cl_2, under otherwise the same conditions, led to a decrease in the *ee* value of **11** from 46 to 39%. Notice that some other metal-catalyzed asymmetric reactions also show significant dependence of enantioselectivity on catalyst loading (see for example: H. M. L. Davies, T. Hansen, M. R. Churchill, *J. Am. Chem. Soc.* **2000**, *122*, 3063).

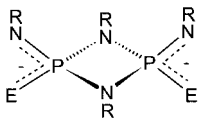
A New Approach to Metalated Imido and Amido Tellurophosphoranes**

Glen G. Briand, Tristram Chivers,* and Masood Parvez

Monoanionic ligands of the type $[R_2P(E)NP(E)R_2]^-$ **1** have been investigated extensively as ligands for both main group elements[1] and transition metals.[2] This widespread interest stems from their potential uses as lanthanide shift reagents,[2] industrial catalysts,[3] luminescent materials,[4] or in metal extraction processes.[5] Recently we[6] and Stahl et al.[7] reported the first ambidentate dianionic ligands $[RN(E)P(\mu\text{-}NR)_2P(E)NR]^{2-}$ **2**, which adopt a variety of bonding modes, that is *N*,*E*, *N*,*N*′, or *E*,*E*′, with metal centers.

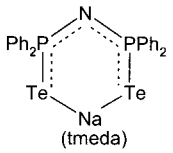


1 (E = O, S, Se)

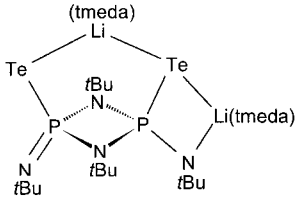


2 (E = S, Se)

Despite this intense activity, the tellurium analogues of **1** and **2** are unknown. Anionic tellurophosphinic amides of the type $[t\text{Bu}_2\text{P(Te)NR}]^-$ (R = *i*Pr, Cy) can be prepared by lithiation of $[t\text{Bu}_2\text{P(Te)NHR}]$ with Li*n*Bu, and chelate complexes of this anion with Group 12 metals have been investigated as single-source precursors of binary metal tellurides.[8] Although ditellurides of the type $[\text{R(Te)P}(\mu\text{-N}t\text{Bu})_2\text{P(Te)R}]$ (R = Me, *t*Bu) have been reported,[9] our attempts to oxidize $t\text{BuN(H)P}(\mu\text{-N}t\text{Bu})_2\text{PN(H)}t\text{Bu}$ with an excess of elemental tellurium in boiling toluene produced only the monotelluride $[t\text{BuNH(Te)P}(\mu\text{-N}t\text{Bu})_2\text{PN(H)}t\text{Bu}]$ in about 5% yield.[10] Endeavors to generate $(\text{TePPh}_2)_2\text{NH}$ in a similar manner have also been unsuccessful. Consequently, we adopted a different approach to the synthesis of the anionic ligands **1** (E = Te) and **2** (E = Te), which involves metalation of the neutral imido or amido precursor prior to the reaction with tellurium.[11] Herein, we report the synthesis and X-ray structures of $[\{[\text{Na(tmeda)}][(\text{TePPh}_2)_2\text{N}]\}_2]$ (**3**) and $[\text{Li(tmeda)}]_2[\text{Te(N}t\text{Bu)P}(\mu\text{-N}t\text{Bu})_2\text{P(N}t\text{Bu)Te}]$ (**4**), (tmeda = tetramethylethylenediamine), which contain the first examples of **1** (E = Te) and **2** (E = Te), respectively.



3



4

The reaction of $\text{Na[Ph}_2\text{PNPPh}_2]$ with tellurium powder in hot toluene in the presence of TMEDA produced **3** as moisture-sensitive, yellow crystals in 33% yield. The molecular structure of **3** (Figure 1) was determined by X-ray diffraction[12] on crystals obtained from hexane. The ditelluroimidodiphosphinate ligand **1** (R = Ph, E = Te) is *Te*,*Te*′ chelated to sodium and forms a centrosymmetric dimer through Na–Te interactions. This is the first example of *Te*,*Te*′ chelation to an alkali metal. The coordination sphere of the Na^+ ions is completed by one *N*,*N*′ chelating tmeda ligand. A similar structure has been reported for the sodium salt of a monothioimidodiphosphinate $[\{\text{Na(thf)}_2[(\text{OPPh}_2)(\text{SPPh}_2)\text{N}]\}_2]$.[13] The central Na_2Te_2 ring in **3** is almost square-planar (bond angles at Na1 and Te1 are 87.51(5) and 92.49(5)°, respectively) with Na–Te distances of 3.143(2) and 3.181(2) Å, which are close to the value of 3.16 Å predicted from the ionic radii[14] and much shorter than the weak Na–Te interactions (3.494(3) Å) in the tellurolate $[\text{Na(tmeda)}_2][\text{Te(2,4,6-Me}_3\text{C}_6\text{H}_2)]$.[15] The P–Te bond lengths of 2.383(1) and 2.403(1) Å are only slightly longer than the values of about 2.37 Å determined for $t\text{Bu}_3\text{P}{=}\text{Te}$[16] and amino-substituted tellurophosphoranes.[9c,17] The shorter P–

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