Crystal structure of an imine–$SnCl_4$ complex. The intermediate in catalytic aziridination reactions

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An imine–$SnCl_4$ complex, which is an intermediate in Lewis acid catalysed aziridination reactions, is isolated and characterised by X-ray diffraction; the structure and catalytic properties of the complex are discussed.

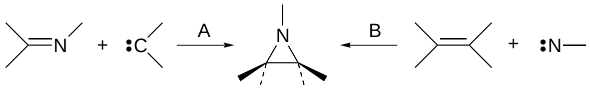
The metal-catalysed aziridination reaction is a new area of organic transformation. Two new catalytic aziridination reactions have been presented within the last few years; one is the metal-catalysed addition of a carbene fragment to an imine (Scheme 1, route A),[1] the other is the addition of a nitrene fragment to an alkene (Scheme 1, route B).[2]

The formation of aziridines from imines and ethyl diazoacetate (EDA) as the carbene-donor fragment (Scheme 1, route A) can take place by two different reaction paths, either by the formation of a metal–carbene, formed by reaction of the metal with EDA with elimination of N_2, then reaction with the imine giving an ylide as the intermediate,[1a,c] or by activation of the imine by the metal—a Lewis acid—followed by a nucleophilic attack by EDA followed by elimination of N_2.[1d,f,h,i]

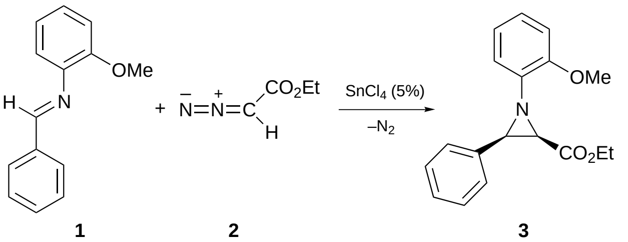
In an attempt to develop a selective aziridination of imines we have turned our attention to potentially bidentate substrates. Here we present the isolation and characterisation of the intermediate in the Lewis acid catalysed aziridination using $SnCl_4$ as the catalyst. This imine–$SnCl_4$ intermediate gives important information about the reaction course for the Lewis acid catalysed aziridination of imines using EDA as the carbene fragment donor.

Reaction of *N*-benzylidine-*o*-anisidine **1** with EDA **2** in the presence of $SnCl_4$ as the catalyst (5 mol%) gives the *cis*-aziridine **3** selectively in reasonable yields (Scheme 2).† In the absence of $SnCl_4$ no reaction takes place.

Choosing imine **1** as the substrate was an attempt to utilise the nitrogen and oxygen lone-pair electrons to give bidentate coordination to the metal. ^{13}C NMR spectroscopic investigations of **1** and $SnCl_4$ in $CDCl_3$ shows a 1:1 complex **4** in solution. The major changes in the ^{13}C NMR chemical shifts of **4**, relative to **1**, are (data in brackets are for **1**): δ 168.6 (161.3), 135.2 (131.2), 131.9 (126.6), 131.2 (128.8), 129.5 (128.6), 113.1 (111.4), 58.1 (55.8). It appears from the ^{13}C NMR data that some of the major changes are in the shifts of the imine and methoxy carbon atoms, from δ 161.3 to 168.6 and from δ 55.8 to 58.1, respectively, by coordination to $SnCl_4$.



Scheme 1



Scheme 2

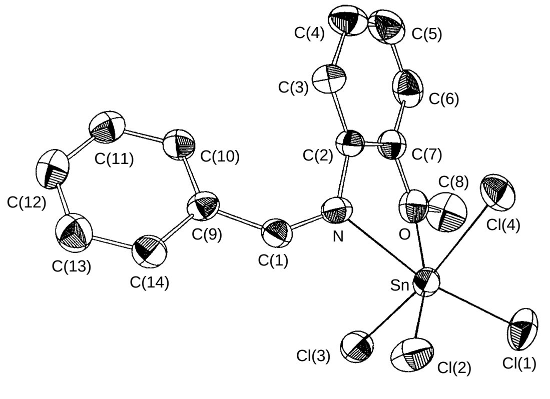
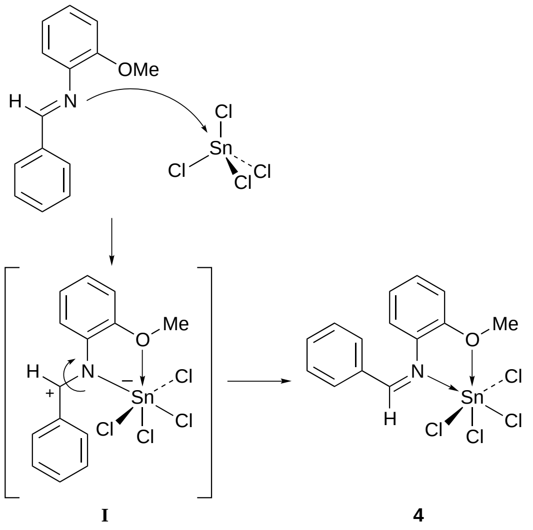


Fig. 1 Molecular structure of **4**. C–H hydrogen atoms are not shown. Selected distances (Å) and angles (°) for **4**: Sn–N 2.222(5), Sn–O 2.370(4), Sn–Cl(1) 2.356(2), Sn–Cl(2) 2.351(2), Sn–Cl(3) 2.372(2), Sn–Cl(4) 2.385(2), N–C(1) 1.285(8), N–C(2) 1.439(7), C(7)–O 1.389(7), O–C(8) 1.439(7), N–Sn–O 68.3(2), Sn–N–C(1) 119.9(4), Sn–N–C(2) 112.8(4), N–C(1)–C(9) 136.0(6), N–C(1)–C(9)–C(10) 8(1), C(1)–N–C(2)–C(3) 47.3(9).

Complex **4** was prepared by the addition of $SnCl_4$ (23.4 mg, 0.20 mmol) to a solution of imine **1** (35.7 mg, 0.20 mmol) in 0.7 ml $CDCl_3$ under Ar. When pale yellow crystals formed the solvent was decanted off to give **4** (50.5 mg, 54%) [mp = 166–72 °C (decomp.)]. The structure of **4**, determined by X-ray diffraction, is depicted in Fig. 1.‡

The structure of **4** consists of the imine **1** coordinated to $SnCl_4$ by the nitrogen and oxygen atoms giving a nearly octahedral geometry at the metal. The X-ray structure shows several interesting structural features, the most remarkable being is the change of geometry of **1**, which in **4** has a *cis*-geometry. The structure of **1** in solution ($CDCl_3$) has been studied by ^1H NMR spectroscopy. A NOEDIF spectrum gives a coupling between the hydrogen atom of the imine and the *ortho*-hydrogen atom in the *o*-anisidine substituent of −3%, showing that **1** is *trans* in solution. The imine **1** isomerises thus by coordination to $SnCl_4$.[3] A mechanism for the *trans* to *cis* isomerisation of **1** by reaction with $SnCl_4$ is proposed in Scheme 3. The first step is a nucleophilic attack of the imine at $SnCl_4$, giving a zwitterion intermediate **I**. The imine part in the zwitterion now has a C–N bond with single bond character which allows rotation, resulting in the *cis* isomer found in **4**. The reason for this isomerisation is probably steric repulsion between the *C*-phenyl substituent and one of the equatorial chlorides. This steric repulsion has been confirmed by modelling of the *trans* isomer of **1** coordinated to $SnCl_4$.

The structural data for **4** presented in Fig. 1 show that the Sn–N and Sn–O bond lengths are 2.222(5) and 2.370(4) Å, respectively, of which the former is similar to the same bond length in the only complex characterised having tin bound to four chlorides and a nitrogen and an oxygen atom.[4] The imine C(1)=N bond in **4** [1.285(8) Å] is not affected by the coordination to $SnCl_4$ and is similar to other imines charac-



Scheme 3

terised.§ The angle between the C(1)–C(9)–C(10)–C(14) and N–C(2)–C(3)–C(7) planes is 48°, which is due to steric repulsion between the two aromatic substituents at the imine.

The 1 : 1.2 reaction between complex **4** and EDA gives the aziridine **3**. However, the isolated yield of **3** is relatively low, caused by the decomposition of the aziridine by $SnCl_4$. Furthermore, we have tried to perform the catalytic reaction of the imine **1** with EDA in the presence of chiral ligands, especially chiral diamines, under various reaction conditions, but racemic **3** was formed. Based on the X-ray structure of **4** and the assumption that the chiral ligand replaces the two equatorial chlorides in **4** modelling studies account for the missing enantioselectivity in aziridination reactions by suggesting that the chiral ligand does not discriminate between the two faces of the imine.

Further work is in progress to understand the catalytic properties of **4** and to develop selective reactions based on this approach.

Footnotes

† *Reaction conditions:* imine 1 (1.0 mmol) was added to a 5 ml Schlenk flask which was evacuated and filled twice with Ar. CH_2Cl_2 (4 ml) was added, followed by $SnCl_4$ or **4** (0.05 mmol). The solution was cooled to −15 °C before the addition of EDA **2** (1.3 mmol). When the evolution of N_2 ceased the reaction mixture was poured onto ice and the resulting aqueous phase was extracted with CH_2Cl_2 (3 ml). The organic phase was washed with 5% aq. $NaHCO_3$ and brine and dried with Na_2SO_4. The crude product was then purified by flash chromatography on silica gel using 5% EtOAc–light petroleum as eluent to give the pure aziridine **3**; δ_H 0.95 (t, *J* 7.2, 3H), 3.09 (d, *J* 6.5, 1H), 3.59 (d, *J* 6.5, 1H), 3.82 (s, 3H), 3.93–4.12 (m, 2H), 6.85–6.89 (m, 2H), 6.94–7.03 (m, 2H), 7.28–7.36 (m, 3H) and 7.54–7.57 (m 2H); δ_C 13.9, 45.9, 47.6, 55.4, 60.8, 111.0, 119.8, 120.6, 123.9, 127.6, 127.8, 127.9, 134.8, 140.8, 152.1 and 168.1; *m/z* 297.133 ($C_{18}H_{19}NO_3$ requires 297.133, 19%), 252 (13) and 224 (100).

‡ *Crystallographic data* for **4**: $C_{14}H_{13}NOCl_4Sn$, monoclinic, space group *C*2/*c*, a = 30.9076(1), b = 7.6820(1), c = 16.3239(1) Å, β = 119.773(1)°, V = 3443.07(7) Å^3, Z = 8; 4361 independent reflections measured at 298 K on a Siemens SMART CCD diffractometer; Mo-Kα; 2750 reflections with $I > 3\sigma(I)$ and 191 variables yields R = 0.038, R_w = 0.052. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/457.

§ A search in the CCDA data file gave for a series of very similar imines an average C=N bond length of 1.28 Å.

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