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Styrene Aziridination by Iron(IV) Nitrides**

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Abstract: *Thermolysis of the iron(IV) nitride complex [PhB(tBuIm)$_3$Fe≡N] with styrene leads to formation of the high-spin iron(II) aziridino complex [PhB(tBuIm)$_3$Fe-N(CH$_2$CHPh)]. Similar aziridination occurs with both electron-rich and electron-poor styrenes, while bulky styrenes hinder the reaction. The aziridino complex [PhB(tBuIm)$_3$Fe-N(CH$_2$CHPh)] acts as a nitride synthon, reacting with electron-poor styrenes to generate their corresponding aziridino complexes, that is, aziridine cross-metathesis. Reaction of [PhB(tBuIm)$_3$Fe-N(CH$_2$CHPh)] with Me$_3$SiCl releases the N-functionalized aziridine Me$_3$SiN(CH$_2$CHPh) while simultaneously generating [PhB(tBuIm)$_3$FeCl]. This closes a synthetic cycle for styrene azirdination by a nitride complex. While the less hindered iron(IV) nitride complex [PhB(MesIm)$_3$Fe≡N] reacts with styrenes below room temperature, only bulky styrenes lead to tractable aziridino products.*

The facile reactivity of aziridines, coupled with their ability to undergo highly regio- and stereoselective transformations, makes them important and versatile synthons in the preparation of small molecules (e.g. pharmaceuticals) and materials (e.g. medical devices).[1] The aziridine moiety is also found in some natural products and synthetic compounds that have interesting or useful biological properties, making them of interest as synthetic targets in their own right.[2]

Given their importance, it is not surprising that numerous schemes for the synthesis of aziridines have been devised.[3] A particularly appealing strategy involves the catalytic transfer of nitrenes to alkenes, which has been extensively investigated and a wide range of metal-based catalysts have been reported.[4] These catalysts include many examples of iron-based complexes that are catalysts for aziridine synthesis by sulfilimine transfer.[5] More recently, the family of iron-based catalysts has been expanded to include complexes that facilitate alkyl- and arylnitrene transfer to styrenes and aliphatic alkenes.[6]

Transition metal nitrides might also be expected to show similar reactivity, in which a two-electron nitrogen atom transfer reaction from the nitride to the alkene leads to formation of a coordinated aziridino ligand. A conceptually attractive feature of such a reaction is that the newly formed aziridino ligand provides a platform for accessing a wider range of N-functionalized aziridines than is possible by current nitrene transfer strategies. However, the majority of nitride ligands are notoriously unreactive, and examples of nitride ligands reacting with hydrocarbons are notable for their rarity.[7] To the best of our knowledge, there is only one example of alkene aziridination by a nitride complex, in which addition of pyridine to the Ru^{VI} nitride complex [(salchda)Ru≡N]$^+$ (salchda = *N*,*N'*-bis(salicylidene)-*o*-cyclohexyldiamine dianion) activates the nitride ligand towards alkene aziridination.[8] A handful of other nitride complexes have been reported to react with alkenes although aziridino ligand formation does not occur, for example, *cis*-[(terpy)Os(N)Cl$_2$]$^+$ inserts the nitrogen atom into the C=C bond of stilbene and conjugated dienes, generating azaallenium products.[9]

In contrast to the low reactivity of most transition metal nitride complexes, the iron(IV) complexes [PhB(RIm)$_3$Fe≡N] (R = *t*Bu **1**, Mes **2**) which are supported by bulky tris(carbene)borate ligands (Figure 1),[10,11] are able to access diverse reaction pathways. Thus, we have chronicled two-electron nitrogen atom transfer reactions to substrates such as C≡O, C≡NR and PR$_3$,[10,11a,12,13] one-electron reactions with hydrogen atom donors and organic radicals,[11b,14] and cycloadditions with conjugated dienes.[14]

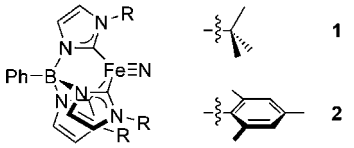

Figure 1. The iron(IV) nitrides [PhB(RIm)$_3$Fe≡N] (R = *t*Bu **1**, Mes **2**).

A detailed experimental and computational investigation into the reaction of **2** with phosphines has provided evidence for the ambiphilic nature of the nitride ligand.[13] An important observation from this study is that the transition state for nitrogen atom transfer involves a σ-symmetry interaction between the nitride LUMO and phosphine

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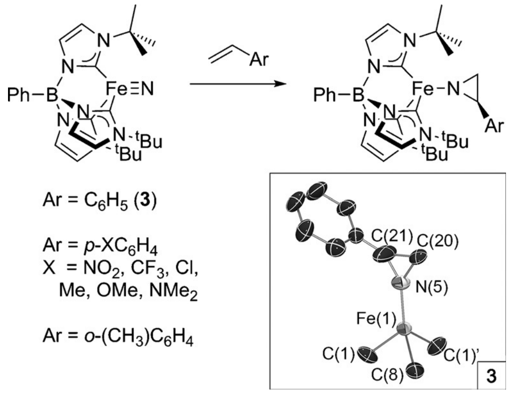
HOMO as well as a π-symmetry interaction between the nitride HOMO and the phosphine LUMO. Since this orbital interaction is reminiscent of bonding between low-valent metals and unsaturated hydrocarbons, we were stimulated to investigate the reactivity of iron(IV) nitrides towards alkenes. Here we report the reactions of **1** and **2** with a range of styrenes, which leads to formation of the corresponding iron(II) aziridino complexes. Evidence for the reversibility of aziridino ligand formation as well as the ability to release an N-functionalized aziridine from the metal is also demonstrated.

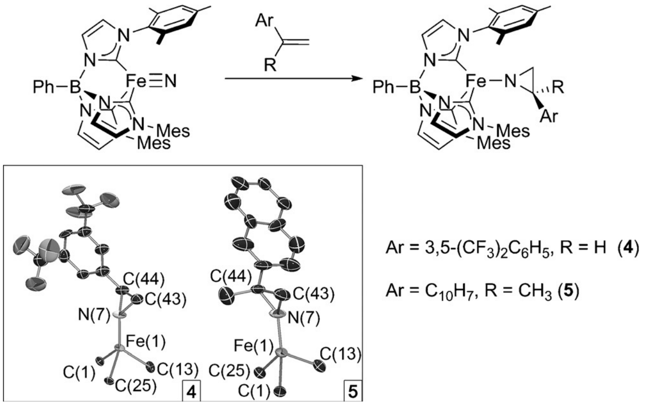
Heating a solution of complex **1** with excess styrene leads to formation of the high-spin ($S = 2$) iron(II) aziridino complex [PhB(*t*BuIm)$_3$Fe-N(CH$_2$CHPh)] (**3**) in high yield (Scheme 1). The molecular structure of **3** has been determined by single-crystal X-ray diffraction (Scheme 1, inset). To the best of our knowledge, this is the first structurally characterized complex featuring an anionic aziridino, rather than neutral aziridine, ligand. The aziridino C(20)−N(5) and C(21)−N(5) bonds of **3** are shorter and the C(20)-N(5)-C(21) bond angle larger than is observed for neutral aziridine ligands, where the corresponding metrics average 1.486(1) Å and 59.5(1.0)°, respectively.[15] As expected from the anionic nature of the aziridino ligand, the Fe(1)−N(5) bond is shorter than observed in iron aziridine complexes[16] but similar to high-spin iron(II) amido complexes.[17] As with the latter complexes, the nitrogen atom of the aziridino ligand in **3** is planar, with the sum of angles around N(5) = 359.9(6)°. The other metrical parameters are unexceptional for a high-spin iron(II) tris(carbene)borate complex.[11–13,18]



Scheme 1. Reaction of **1** with a range of styrenes, leading to formation of the corresponding aziridino complexes. Inset: X-ray crystal structure of **3**, where Ar = C$_6$H$_5$. Thermal ellipsoids at 50%, hydrogen atoms and most of the tris(carbene)borate ligand omitted for clarity. Fe(1)–N(5) 1.935(4); Fe(1)–C(1) 2.092(4); Fe(1)–C(8) 2.109(6); N(5)–C(20) 1.417(11); N(5)–C(21) 1.317(14); C(20)–C(21) 1.476; C(1)-Fe(1)-C(8) 90.58(16); Fe(1)-N(5)-C(20) 142.0(5); Fe(1)-N(5)-C(21) 152.5(6); C(20)-N(5)-C(21) 65.3(6).

Complex **1** reacts similarly with other styrenes, although the reaction is sensitive to the size of the styrene substrate. While all *para*-substituted styrenes investigated provide the corresponding aziridino complexes, as do *o*-(CH$_3$)C$_6$H$_4$C(H)=CH$_2$ and C$_{10}$H$_7$CH=CH$_2$, there is no reaction with the bulkier styrene 2,4,6-(CH$_3$)$_2$C$_6$H$_3$C(H)=CH$_2$. In addition, no reaction between **1** and β-substituted styrenes, for example, C$_6$H$_5$-C(H)=C(H)CH$_3$, is observed.

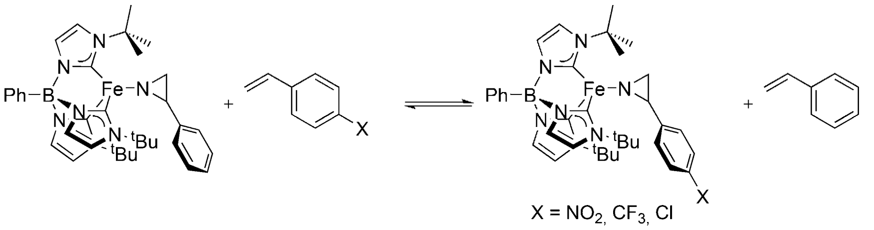
While the reactions of nitride complex **1** generally require heat, complex **2** reacts with styrenes under ambient conditions. Thus, **2** reacts at room temperature with 3,5-(CF$_3$)$_2$C$_6$H$_3$CH=CH$_2$ and C$_{10}$H$_7$C(CH$_3$)=CH$_2$ to afford the corresponding high-spin iron(II) aziridino complexes **4** and **5** as the sole reaction products (Scheme 2). These complexes have also been structurally characterized, showing similar metrical parameters to **3**, except for significant pyramidalization of the aziridino nitrogen atom (sum of angles around N(7) = 336.2(9)° and 348.2(4)° for **4** and **5**, respectively). While **2** reacts with these bulky styrenes under very mild conditions, even below room temperature, the reaction scope of this complex is generally more limited than that of **1**, with less bulky styrene substrates leading to the formation of intractable products.



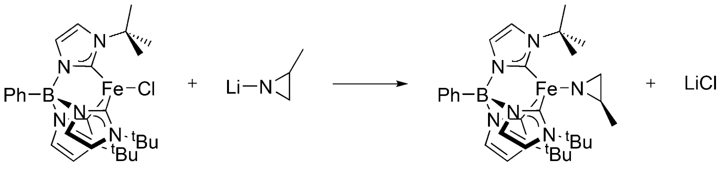
Scheme 2. Reaction of **2** with bulky styrenes to afford the corresponding aziridino complexes **4** and **5**. Inset: X-ray crystal structures of **4** (left) and **5** (right). Thermal ellipsoids at 50%, hydrogen atoms and most of the tris(carbene)borate ligand omitted for clarity.

These synthetic results therefore establish an unusual transformation for a nitride ligand, in which two-electron nitrogen atom transfer to styrenes provides the corresponding aziridino complexes. As mentioned above, there are a handful of transition metal nitride complexes that react with alkenes,[9] and in only one instance does a two-electron nitrogen atom transfer reaction occur to generate the three-membered aziridine ring.[8]

Intriguingly, the aziridino complex **3** can be used as an iron(IV) nitride synthon. Specifically, heating **3** with (*p*-NO$_2$C$_6$H$_4$)CH=CH$_2$ leads to formation of the aziridino complex [PhB(*t*BuIm)$_3$Fe-N(CH$_2$CH(*p*-(NO$_2$)C$_6$H$_4$))] and styrene, that is, aziridine cross-metathesis (Scheme 3). Similar aziridine cross-metathesis occurs when **3** is treated with electron-poor styrenes such as (*p*-ClC$_6$H$_4$)CH=CH$_2$ and (*p*-CF$_3$C$_6$H$_4$)CH=CH$_2$, although no reaction occurs with more electron-rich styrenes. While detailed studies aimed at elucidating the aziridination mechanism are ongoing, this cross metathesis reactivity strongly suggests the aziridination reaction to be reversible.



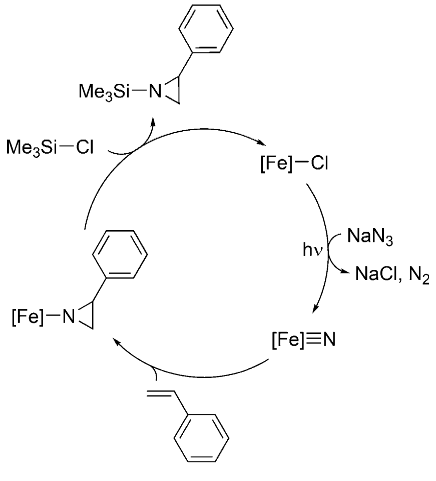
Scheme 3. Aziridine cross-metathesis.



Scheme 4. Synthesis of [PhB(*t*BuIm)$_3$Fe-N(CH$_2$CHCH$_3$)] (**6**).

In contrast to the reactions with styrenes, which lead to aziridino ligand formation, neither nitride complex reacts with aliphatic alkenes. However, it is possible to independently prepare an iron(II) aziridino complex that would result from such a reaction. Treating [PhB(*t*BuIm)$_3$FeCl] with [LiN(CH$_2$CHCH$_3$)] yields the corresponding aziridino complex [PhB(*t*BuIm)$_3$Fe-N(CH$_2$CHCH$_3$)] (**6**) in high yield (Scheme 4). This complex, which has also been structurally characterized,[15] shows no propensity for releasing propene under thermal or photochemical conditions, nor does it undergo aziridine cross-metathesis reactions with added styrenes. These results therefore suggest that a kinetic barrier prevents the iron nitrides from accessing similar aziridination reactivity with aliphatic alkenes.

As suggested at the outset, the iron(II) aziridino complexes have potential application as synthons for a range of N-functionalized aziridines. In a proof-of-concept experiment, treating the aziridino complex **3** with one equivalent Me$_3$SiCl leads to quantitative formation of the iron(II) complex [PhB(*t*BuIm)$_3$FeCl] and the corresponding N-silylated aziridine Me$_3$SiN(CH$_2$CHPh). To the best of our knowledge, N-silylated aziridines are not accessible by current nitrene transfer strategies.[19] In addition, since the iron(II) chloride complex is readily converted to **1**,[18] this reaction establishes a synthetic cycle for styrene aziridination using an iron(IV) nitride (Scheme 5). Preliminary results suggest that access to other N-functionalized aziridines will be similarly facile, as illustrated by the synthesis of the N-methylated aziridine MeN(CH$_2$CHPh) by reaction of **3** with MeI.



Scheme 5. Synthetic cycle for styrene aziridination by an iron(IV) nitride complex.

In summary, the reactivity of a suitable iron(IV) nitrides allows a cycle for the synthesis of N-functionalized aziridines to be developed. Work to investigate the mechanism of the aziridination reaction is underway, as are efforts to develop catalytic cycles for the synthesis of range of N-functionalized aziridines using iron(IV) nitride complexes.

Keywords: alkenes · iron · nitrides

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