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Probing the role of an Fe^{IV} tetrazene in catalytic aziridination[†]

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An iron(v) tetrazene complex has been synthesized that is an important addition to a previously proposed catalytic aziridination cycle. It provides two key insights about the aziridination: an iron(v) imide is formed and this imide can bind an additional ligand in the *cis* position.

The synthesis of non-heme iron(*iv*) complexes has been of considerable interest due to their roles in biomimetic chemistry as well as catalytic group transfer reactions.^{1,2} Iron(*iv*) oxo complexes, prepared by Que,³ Borovik,⁴ and Nam,⁵ have been shown to be effective at O-atom transfer. Likewise, iron(*iv*) nitrides have been considered as intermediates in the formation of ammonia from dinitrogen.^{6,7} Finally, several iron(*iv*) imide complexes have been prepared and implemented for a variety of nitrene transfer reactions.^{8,9} In all cases, even when the iron(*iv*) complex cannot be isolated, these intermediates are often considered reactive species in catalytic cycles.^{10,11}

When we previously reported an atom economical $C_2 + N_1$ aziridination with $[(^{Me,Et}TC^{Ph})Fe(NCCH_3)_2](PF_6)_2(1)$ as the catalyst, we detected a transient imide species, $[(^{Me,Et}TC^{Ph})Fe=NAr]^{2+}$ (Ar = aryl) by electrospray ionization mass spectrometry (ESI-MS).¹² Based on this result, and the later synthesis of $[(^{Me,Et}TC^{H})Fe(O)(NCCH_3)]^{2+}$, a terminal Fe^{IV} oxo, by Meyer¹³ we believed that it would be possible to isolate a stable Fe^{IV} imido to study the aziridination reaction in a step-wise manner, which may lead to greater elucidation of the mechanism. Despite considerable effort, we have been unable to isolate $[(^{Me,Et}TC^{Ph})Fe=NAr]^{2+}$. Instead, even at relatively low temperatures, two equivalents of organic azide react with 1 to form the corresponding iron tetrazene, $[(^{Me,Et}TC^{Ph})Fe((p-tolyl)N_4(p-tolyl))]$ -(PF₆)₂ (2) (Scheme 1). Tetrazenes are famous examples of non-innocent ligands that are usually formed by addition of an organic azide to a metal imide in a [2+3] cycloaddition.^{14–16} While Trogler noted early examples "defy a simple description",¹⁷ they have since been classified into three groups by Holland¹⁸ that allow for the determination of bonding mode to the metal center. Well-characterized iron tetrazene complexes have recently been prepared by Holland and Riordan,^{18,19} but the reactivity of iron tetrazene complexes have necessary tetrazene complexes have necessary tetrazene complexes. This communication presents the first example of an iron(n) tetrazene complex, which is also a component of a catalytic aziridination cycle. This novel complex is both fully characterized structurally and spectroscopically, and its reactivity provides insight into the aziridination catalytic cycle.

Addition of tolyl azide to **1** at 40 °C resulted in formation of $[(^{Me,Et}TC^{Ph})Fe((p-tolyl)N_4(p-tolyl))](PF_6)_2$ (2), in a 74% isolated crystalline yield. As previously discussed by Gade and Holland,^{18,20} metallotetrazenes are generally formed by a [2+3] cycloaddition of an additional equivalent of organic azide to the metal imide (Scheme 1). Unlike the six-coordinate $[(^{Me,Et}TC^{H})Fe(O)(NCCH_3)](OTf)_2$ (OTf = triflate),¹³ where *S* = 1, complex 2 was found to be diamagnetic (*S* = 0) at room temperature. ¹H NMR exhibits diastereotopism at the methylene and ethylene protons of the N-heterocyclic carbene (NHC) linkers that is consistent with several other rigid tetracarbene complexes that we have synthesized.^{21–23} Notably, the ¹³C NMR showed a resonance for the carbene carbon at 169.79 ppm that is shifted significantly upfield (~26 ppm) from 1.¹²

The X-ray crystal structure of **2** confirms the formation of an iron tetrazene complex (Fig. 1A). Notably, **2** adopts a trigonal prismatic geometry with a slight twisting distortion ($\phi_{Ave} = 10.4^{\circ}$) as opposed to the octahedral geometry seen in **1** (trigonal prismatic, $\phi = 0^{\circ}$; octahedral, $\phi = 60^{\circ}$).²⁴ While there are several examples of trigonal prismatic Fe^{II} complexes,^{25,26} there are only a few Fe^{III} examples,²⁷ and to date no examples with Fe^{IV} have been synthesized. The trigonal prismatic geometry is favorable since this reduces steric interactions between the aryl rings on the tetrazene and the aryl rings on the tetracarbene macrocycle. The average Fe–NHC bond length is 1.98 Å, which is slightly

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Scheme 1 Reaction cycle of aziridination showing purported imide intermediate (center) and isolated tetrazene complex 2 (right).



Fig. 1 (A) X-ray crystal structure of **2** from a top down view. (B) X-ray crystal structure of **2** from a side view with selected parts of the macrocycle omitted for clarity. Orange, blue and grey ellipsoids (50% probability) represent Fe, N and C, respectively. H atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å): Fe-C₁, 1.952(3); Fe-C₂, 1.987(3); Fe-C₃, 1.954(3); Fe-C₄, 2.011(2); Fe-N₉, 1.896(2); Fe-N₁₂, 1.921(2), N₉-N₁₀, 1.345(3); N₁₀-N₁₁, 1.292(3); N₁₁-N₁₂, 1.343(3). (C) Mössbauer spectrum of **2**: δ , $|\Delta E_{\rm o}|$ (mm s⁻¹): -0.01, 0.62.

shorter than the average bond length for **1**, but is in line with Meyer's octahedral Fe^{IV}-oxo tetracarbene complex.¹³

A close examination of the X-ray crystal structure demonstrates two notable points. First, the crystal structure provides a hint as to a possible mechanism for aziridination from the Fe-imide intermediate. Since the alkene must be present near the metal imide prior to group transfer, the tetracarbene ligand then must be flexible enough to accommodate an additional ligand in a *cis* position which is well illustrated by the formation of 2 (Fig. 1B). Second, the X-ray structure can help deduce the oxidation state of the iron center *via* careful evaluation of the N–N bond lengths of the tetrazene ligand. The N₁₀–N₁₁ bond length is 1.292(3) Å which is shorter than the N₉–N₁₀ or N₁₁–N₁₂ bond lengths (1.345(3) and 1.343(3), respectively) suggesting that the central nitrogens have a double bond. This double bond is indicative of a dianionic tetrazene ligand, which is suggestive of an Fe^{IV} metal center. In contrast, a previously reported Fe^{II}-tetrazene by Holland adopts a radical anion binding mode where the radical is based at the tetrazene ligand, but the noninnocent tetrazene ligand does adopt a dianionic binding mode upon chemical reduction.¹⁸

In order to confirm the nature of **2** as a low spin (S = 0) Fe^{IV} complex, zero field 57Fe Mössbauer spectroscopy was collected on this species. Iron(IV) species investigated by Mössbauer spectroscopy range in isomer shifts from as negative as -0.34to as positive as 0.18 mm s⁻¹, ^{3,11,28} In particular, two examples of Fe^{IV} complexes have been isolated and investigated with polydentate carbene ligands, a nitride by Smith and an oxo by Meyer.^{13,29} The spectrum of 2 (Fig. 1C) shows an isomer shift (δ) of -0.01 mm s^{-1} and quadrupole splitting ($|\Delta E_{O}|$) of 0.62 mm s⁻¹, which is consistent with a low spin Fe^{IV} metal center. The combination of diamagnetism observed in NMR (with ¹³C carbene shift), short N110-N11 bond distance, and Mössbauer spectroscopy, demonstrates that the tetrazene ligand in 2 is a dianionic ligand and the iron is in a tetravalent low spin state. Based on both structural and spectroscopic evidence collected, we conclude that 2 is the first example of a trigonal prismatic Fe^{IV} complex.

Because tetrazene ligands are often non-innocent, we interrogated whether the redox behavior of 2 was metal or ligand based. Cyclic voltammetry shows a single reversible reduction wave centered at -1.05 V *versus* ferrocene in an acetonitrile solution. Complex 2 was reduced with one equivalent of cobaltocene yielding [(^{Me,Et}TC^{*Pt*})Fe((*p*-tolyl)N₄(*p*-tolyl))](PF₆) (3). The X-ray structure



Fig. 2 (A) X-ray crystal structure of **3** from a top down view. Orange, blue and grey ellipsoids (50% probability) represent Fe, N and C, respectively. H atoms, counteranions, and solvent molecules have been removed for clarity. Selected bond lengths (Å): Fe-C₁, 1.963(3); Fe-C₂, 1.963(3); Fe-C₃, 1.976(3); Fe-C₄, 1.958(3); Fe-N₉, 1.947(2); Fe-N₁₂, 1.980(2), N₉-N₁₀, 1.368(3); N₁₀-N₁₁, 1.272(3); N₁₁-N₁₂, 1.377(3). (B) Mössbauer spectrum of **3**: δ , $|\Delta E_{\rm Q}|$ (mm s⁻¹): 0.10, 1.13. (C) Frozen solution EPR of **3** at 77 K: $g_{\parallel} = 2.094(1)$, $g_{\perp} = 1.997(1)$.

of **3** reveals the same general geometry about the metal center (Fig. 2A) except the dihedral angle (ϕ) has increased to 22.1°. The central N–N bond distance in **3** is significantly shorter (about 0.10 Å) than the peripheral N–N bond distances suggesting that the tetrazene ligand remained dianionic.

The spectroscopic data for 3 also shows that the tetrazene is in the dianionic binding mode in the reduced state. The Mössbauer spectrum of 3 is shifted to a more positive isomer shift relative to its Fe^{IV} congener, consistent with an Fe^{III} state (Fig. 2B).^{13,30} More tellingly, the EPR spectra of 3 shows an axial pattern with $g_{\parallel} = 2.094(1)$ and $g_{\perp} = 1.997(1)$ consistent with a low spin (S = 1/2) Fe^{III} (Fig. 2C).³¹ This EPR spectrum is distinct from Wagner's trigonal prismatic Fe^{III} complexes,²⁷ which are high spin, as well as the other iron tetrazenes of Riordan and Holland.^{18,19} Unlike their results with iron tetrazenes, we have found the ligand behaves in a fully "innocent" manner regardless of Fe oxidation state.

Due to 1 being an excellent aziridination catalyst and since 2 is formed by addition of excess organic azide to 1, the question arose as to whether 2 was a competent catalyst for aziridination or whether it was a poison to the catalytic cycle. We performed both stoichiometric and catalytic tests with 2 to probe its role in the aziridination catalytic cycle. Our initial reaction was to try to reform 1 by removing the tetrazene ligand by thermal decomposition (Fig. S1, ESI†). Previous thermolysis reactions with metallotetrazenes have noted the extrusion of N_2 ,¹⁷ yet the only noted by-product of such reactions were the respective diimide

complexes,³⁰ not the subsequent nitrene coupling. Hillhouse and Cundari implicated a metallotetrazene as the intermediary step (based on DFT calculations) in the conversion of a Ni(π) imido to form diazene derivatives, although they did not report any experimental evidence for the tetrazene intermediate.³² Although several catalysts have been successful in the conversion of organic azides to diazene, including a recent example by Peters, none of these examples have been proposed to proceed through a tetrazene intermediate.^{33–35} Heating 2 at 85 °C in CD₃CN formed 1 and 4,4'-dimethylazobenzene after 24 hours (Scheme 1). This result is significant because it shows that 1 can be regenerated below the temperature at which we perform aziridination catalysis. In addition, we believe that this is the first well-characterized step-wise formation of an azobenzene from a metallotetrazene.

Since we could reform **1**, we believed that **2** would also be a competent catalyst for aziridination. Addition of cyclooctene and *p*-tolyl azide in a 20:1 ratio to 2 (at 0.2% catalyst loading) gave a 77% yield of 9-(*p*-tolyl)-9-azabicyclo[6.1.0]nonane by NMR integration with an internal standard (less than 5% 4,4'-dimethylazobenzene was formed during the catalysis). These results encouraged us to inquire whether direct group transfer could occur from the tetrazene ligand on **2**. Heating **2** in neat cyclooctene at 90 °C formed a mixture of both 4,4'-dimethylazobenzene and 9-(*p*-tolyl)-9-azabicyclo[6.1.0]nonane in a 2.3:1 ratio respectively, based on NMR integration (Fig. S2, ESI†). Since multiple products are formed from **2**, it appears that multiple reaction mechanisms occur simultaneously at this temperature. To our knowledge, this is the first example of formation of an aziridine from a metallotetrazene.

In conclusion, we have synthesized the first iron(IV) tetrazene complex, $[(^{Me,Et}TC^{Ph})Fe((p-tolyl)N_4(p-tolyl))](PF_6)_2$, which has been found to be an important component of our catalytic cycle for aziridination. The complex is low spin and in a trigonal prismatic geometry and based on spectroscopic and structural data the tetrazene binds in the dianionic mode. The X-ray structure demonstrates a key point that is salient to this unique catalytic cycle, namely that the macrocyclic tetracarbene is flexible enough to allow an alkene to bind in a cis position prior to loss of aziridine. The iron(IV) tetrazene complex will release 4,4'-dimethylazobenzene allowing for the regeneration of the original catalyst and is itself a competent starting point for catalytic aziridination. Perhaps more remarkably, the tetrazene will yield 9-(p-tolyl)-9-azabicyclo[6.1.0]nonane (as well as 4,4'-dimethylazobenzene) in the presence of excess cyclooctene which has not been previously demonstrated. These combined results suggest that an iron(iv) imide is formed during catalysis.

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