Homogeneous Catalysis

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Correlation of Metal Spin State with Catalytic Reactivity: Polymerizations Mediated by α-Diimine–Iron Complexes**

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It has long been recognized that the metal spin state plays a central role in the reactivity of important biomolecules such as the heme-based metalloproteins.[1–5] In nonbiological systems the connection between metal spin state and reactivity, especially in catalysis, has remained largely undeveloped. Herein, we describe a homogeneous catalytic system in which closely related iron complexes with differing metal spin states afford starkly contrasting mechanistic outcomes in catalytic polymerization, to our knowledge the first time such distinct catalytic reaction pathways have been delineated for metal spin state isomers outside a biological manifold.

Four-coordinate α-diimine iron complexes $[^{R}(N,N)FeCl_2]$ ($^{R}(N,N)$ = RN=CH−CH=NR) have previously been shown to be active as atom transfer radical polymerization (ATRP) catalysts for the controlled polymerization of styrene.[6,7] In our initial studies, we were surprised to find that ATRP predominates in reactions catalyzed by alkylimine derivatives whereas those catalyzed by arylimine complexes give rise to polymers in which catalytic chain transfer (CCT) is dominant.

Atom transfer radical polymerization is a versatile and increasingly exploited methodology for the synthesis of novel materials by controlled radical polymerization.[8] It involves a dynamic equilibrium between growing and dormant polymer chains using a metal-mediated halogen-exchange process. By ensuring the equilibrium is shifted towards the dormant species, radical concentrations remain low, reducing bimolecular termination and generating polymers with well-defined molecular weights that increase linearly with conversion. If the organoradicals are trapped by the Fe^{II} complex, then an organometallic species is generated which can undergo a β-hydrogen elimination reaction to give short chain, olefin-terminated oligomers, with molecular weights largely independent of conversion. This process is termed catalytic chain transfer.

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The observed polymerization mechanism is determined by the competition between the equilibria shown in Figure 1,[9] which may be viewed as arising from the differing halogenophilicities and carbophilicities of the Fe^{II} species, where halogenophilicity and carbophilicity can be defined as the relative predilection for a complex to form metal–halogen and metal–carbon bonds, respectively. In ATRP, an equilibrium is established between Fe^{II} dichloride and Fe^{III} trichloride complexes. The propensity for Fe^{II} complexes to react with a chloroalkane to form the oxidized species and a carbon radical is a function of its halogenophilicity. One mechanism by which catalytic chain transfer may occur involves the formation of a metal–carbon bond, followed by β-hydrogen elimination to generate an alkene-terminated polymer chain. If such a mechanism were operating, it would imply the presence of a second equilibrium in which the dormant Fe^{II} dichloride can trap and stabilize the free radical to form an Fe^{III} alkyl dichloride. The analogous idiom for this equilibrium can be termed carbophilicity.

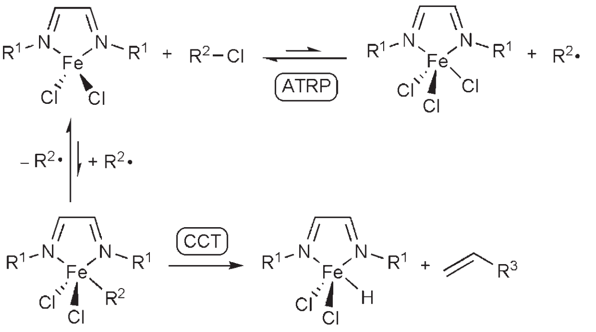

Figure 1. Equilibria involved in ATRP versus CCT polymerization (ATRP = atom transfer radical polymerization, CCT = catalytic chain transfer).

To investigate the origin of the differing polymerization mechanisms of these iron catalysts, the trivalent derivatives [^{R}(*N,N*)$FeCl_3$] (R = cyclohexyl (Cy), **1**; *t*Bu, **2**; 2,6-*i*$Pr_2C_6H_3$ (DIPP), **3**) were prepared by addition of the α-diimines to $FeCl_3$. For **1**, a solution magnetic moment of 5.97 μ_B was obtained, corresponding well with the spin-only value of 5.92 μ_B for a d^5 high-spin iron(III) center (S = 5/2, sextet). The magnetic moment for **3** (3.99 μ_B) corresponds well to a d^5 intermediate-spin iron(III) center (3.87 μ_B, S = 3/2, quartet).[10] While intermediate-spin iron(III) is rare in biological systems,[11,12] numerous iron porphyrinogen and porphyrin complexes exist in quartet spin states.[13–15] This trend persists in other [^{R}(*N,N*)$FeCl_3$] complexes; aliphatic α-diimines have high-spin magnetic moments while lower spins are observed in aromatic systems. This difference correlates well with the observed polymerization behaviour; alkylimine iron complexes behave as ATRP catalysts, but arylimine systems promote CCT. Could this change in spin state account for the apparent change in halogenophilicity versus carbophilicity and thus determine the outcome of the polymerization?

All [^{R}(*N,N*)$FeCl_2$] complexes react cleanly with R–Cl species under polymerization conditions to give coupled products and the corresponding Fe^{III} species, illustrating the halogenophilic reactivity of each species. To probe the relative carbophilicity of [^{R}(*N,N*)$FeCl_2$] complexes, the mono-benzyl Fe^{III} complexes, [^{R}(*N,N*)$FeBnCl_2$] (Bn = CH_2Ph), were targeted. Addition of BnMgCl at −78 °C to **1** produced an immediate color change from yellow to deep purple, and [^{Cy}(*N,N*)$FeCl_2$] was isolated from the reaction mixture. GC analysis of the reaction products indicated the formation of bibenzyl (Bn_2, $PhCH_2CH_2Ph$) via the coupling of two alkyl radicals formed from the reductive alkylation of **1**. Similarly, alkylation of **2** produced bibenzyl at very low temperatures. The iron–carbon bond is unstable, generating carbon radicals in solution which couple to form the observed product.

The reaction of **3** with BnMgCl at −78 °C produced a markedly different result. GC analysis, after hydrolysis, showed that toluene was the major product, not bibenzyl. Upon warming the solution to −20 °C, a green-black to red color change coincided with the formation of bibenzyl, now the major decomposition product. The radical coupling occurs at a much higher temperature, implying that the alkyl complexes have improved stability. The graph in Figure 2 shows the ratio of bibenzyl/toluene formed as a function of temperature. Formation of bibenzyl predominates even at −78 °C when R = Cy (≈7.5 Bn_2/toluene), but toluene outweighs bibenzyl for R = DIPP (≈0.2 Bn_2/toluene) until −20 °C when decomposition occurs (≈5.5 Bn_2/toluene). It is clear that the aryl derivative has improved thermal stability; thus complex **3** is a better alkyl radical trap at low temperatures and therefore may be viewed as being more carbophilic. At polymerization temperatures, where all Fe^{III} species are transient, this increased stability will result in a shift in the relative positions of the equilibria in Figure 1. These experimental observations support the notion that the diisopropylphenyl derivative is more carbophilic and thus a better CCT catalyst than either of the cyclohexyl or *tert*-butyl derivatives. The lower-spin-state complexes will also have a vacant metal d orbital available to facilitate the subsequent β-hydrogen-elimination process.

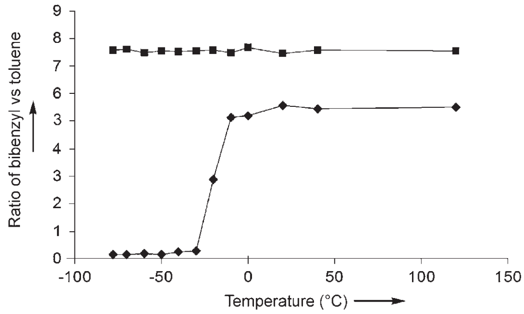

Figure 2. Ratio of integrated GC peaks for the formation of bibenzyl and toluene arising from the decomposition of [^{R}(*N,N*)$FeCl_2(CH_2Ph)$] at different temperatures; R = Cy (■), R = DIPP (◆). Higher ratios indicate bibenzyl is the primary decomposition product. Ratios below 1 indicate toluene is the primary decomposition product.

To learn more about the role of metal spin state, a series of Hartree–Fock-level all-electron [ROHF/6-31G(3d)] calculations were performed on model systems for the two competing reactions of $[^{R}(N,N)FeCl_2]$. The chosen basis set effectively reproduces core geometries of first-row transition-metal systems while ensuring reasonable calculation times.[16] Entropic differences required for Equation (2) are estimated by using the model system $CCl_2 + PhCH_2^{\cdot} \rightleftharpoons PhCH_2CCl_2^{\cdot}$. Previous studies[17–19] have shown that the choice of basis set and correlation treatment has a major influence on the relative stabilities of sextet and quartet states in iron systems. Although ROHF calculations overestimate the stability of the sextet state, producing large energy differences between sextet and quartet systems, they more accurately reproduce energy differences between two self-consistent sextet complexes.

Reactions (1) and (2), in which R is either *t*Bu or Ph, were

$$[^{R}(N,N)FeCl_2] + C_6H_5CH_2Cl \rightleftharpoons [^{R}(N,N)FeCl_3] + C_6H_5CH_2^{\cdot} \quad (1)$$

$$[^{R}(N,N)FeCl_2] + C_6H_5CH_2^{\cdot} \rightleftharpoons [^{R}(N,N)FeCl_2(CH_2C_6H_5)] \quad (2)$$

computed with the spin state of the iron complexes specified as either quartet ($S=3/2$) or sextet ($S=5/2$) for the Fe^{III} species. The relative preference of the two reactions for a particular spin state of iron is a determinant of carbophilicity versus halogenophilicity. For Fe^{III} sextet systems, halogenophilic behavior is favored. For R = *t*Bu and Ph, Reaction (1) is favored over Reaction (2) by 10.6 and 5.5 kcal mol^{-1}, respectively. This trend, however, is reversed for intermediate-spin quartet systems. For R = *t*Bu and Ph, Reaction (2) is now favored by 0.9 and 4.6 kcal mol^{-1}, respectively. The calculations thus predict that systems with $S=3/2$ spin states are carbophilic while those with $S=5/2$ spin states are halogenophilic. The calculations also show that for R = Ph the carbophilicity is even more pronounced, supporting the experimental evidence for arylimine carbophilicity.

An orbital correlation study between $[^{tBu}(N,N)FeCl_3]$ sextet and quartet spin states suggests a rationale for the preference of intermediate spin states for arylimines. The quartet is formally linked to the sextet state by a single electron promotion, and this directly impacts upon the occupied orbital energies and their propensity to include mixing with other atomic orbitals (AOs). In the sextet state, molecular orbital (MO) 84 is singly occupied and predominantly Fe d AO in character with little other mixing. In the quartet state, this MO becomes doubly occupied with a resulting lower energy (61). This introduces metal-based d AOs mixing with ligand AOs of similar energy, creating a delocalized MO in which conjugation with the α-diimine is a prominent feature. This coupling suggests that changes to the electronic characteristics of the ligand substituents would have a strong influence on the nature of the quartet orbital (Figure 3) and hence the quartet/sextet balance.

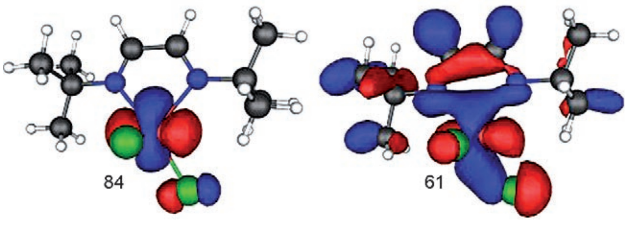

Figure 3. Selected orbital correlation between the singly occupied orbital in the $[^{tBu}(N,N)FeCl_3]$ sextet (orbital 84, left) and doubly occupied orbital in the corresponding quartet (orbital 61, right).

As the conjugation of this orbital into the ligand backbone includes the 2 and 3 positions of the backbone, these sites will also affect the quartet state and its promotion to a sextet state. Systematic alteration of the backbone substituents should, therefore, control the metal spin state and thus catalyst behavior without significant alteration of the steric environment at the iron center. To tune the catalyst for halogeno- or carbophilicity, $[^{R}(N,N)FeCl_2]$ complexes were targeted containing an electron-withdrawing *para*-fluorophenyl group at the 2 and 3 positions of the ligand backbone. Syntheses of $[tBuN{=}C(C_6H_4F)]_2$ (**4**) and $[CyN{=}C(C_6H_4F)]_2$ (**5**) were accomplished by condensation of the requisite amine with *para*-fluorobenzil, activated by $TiCl_4$.[20] Reaction of **4** or **5** with $FeCl_2{\cdot}1.5\,THF$[21] generated $[^{tBu,FC_6H_4}(N,N)FeCl_2]$ (**6**) and $[^{Cy,FC_6H_4}(N,N)FeCl_2]$ (**7**). The atom transfer radical polymerization of styrene initiated using 1-phenylethyl chloride (1-PECl) with $[^{Cy}(N,N)FeCl_2]$ and $[^{tBu}(N,N)FeCl_2]$ at 120 °C is characterized by low polydispersities and molecular weights that increase linearly with time and conversion.[4] The polymerization of styrene using the aryl-substituted catalysts **6** and **7** monitored under the same conditions generates polymer through a different mechanism. The reactions proceed relatively slowly (e.g. for **6**, $k_{obs.} = 0.02\ h^{-1}$) and the polymer obtained was of low molecular weight (Figure 4).

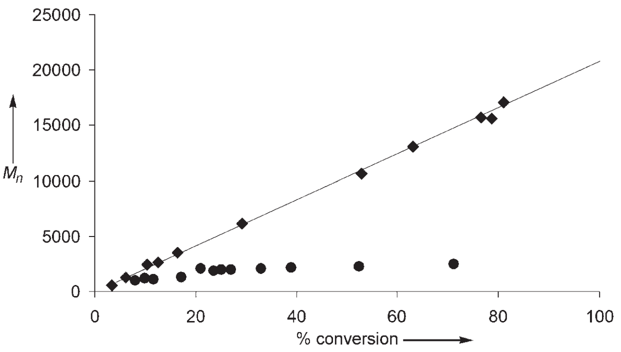

Figure 4. Plot of molecular weight, M_n, versus conversion for polymerization of styrene by $[^{tBu}(N,N)FeCl_2]$ (◆) and $[^{tBu,FC_6H_4}(N,N)FeCl_2]$ (●).

End-group analysis by multinuclear NMR spectroscopy confirmed that olefin-terminated polymer had formed. The polymerization mechanism has switched, generating low molecular weight polymer presumably by a catalytic chain transfer mechanism. Synthesis of the Fe^{III} complexes $[^{tBu,FC_6H_4}(N,N)FeCl_3]$ (**8**) and $[^{Cy,FC_6H_4}(N,N)FeCl_3]$ (**9**) established that control over metal spin state has been achieved. The two complexes have solution magnetic moments of 4.01 and 3.85 μ_B, respectively, indicating that both are intermediate-spin $S=3/2$ systems. Evans' method NMR spectroscopic measurements over the temperature range 18–120 °C confirmed that the intermediate spin state prevails at the polymerization temperature.

In summary, we have demonstrated a correlation between metal spin state and a simple catalytic chemical reaction, that of polymerization. For Fe^{III} species in a high spin state ($S = 5/2$), living atom transfer radical polymerization predominates, whereas with catalysts in an intermediate spin state ($S = 3/2$), an organometallic pathway leads to catalytic chain transfer. We have further shown that the metal spin state of the iron species can be controlled by judicious choice of α-diimine ligand substituents, highlighting the possibilities for the rational design of catalysts on the basis of metal spin state.

Experimental Section

All solvents were distilled over standard drying agents under nitrogen and were deoxygenated before use. All reactions were performed under an inert atmosphere. Full experimental and calculation details, as well as characterization and polymerization data can be found in the Supporting Information.

Ligand synthesis: To a solution of the appropriate amine (80.0 mmol) in CH_2Cl_2 (30 mL) at 0 °C was added dropwise $TiCl_4$ (1.0 M in CH_2Cl_2, 12.2 mL, 12 mmol). *p*-Fluorobenzene (2.5 g, 10 mmol) in CH_2Cl_2 (10 mL) was added dropwise, and the solution allowed to warm to room temperature and stir overnight. The reaction was quenched with water, filtered, and extracted into CH_2Cl_2. Removal of solvent left a sticky orange solid, which was recrystallized from MeOH (60 mL) to give off-white crystals of **4** (3.06 g, 84 %) and **5** (3.65 g, 88 %), respectively. Other diimine ligands were prepared as described in the literature.[22,23]

$[^{R}(N,N)FeCl_n]$ synthesis: To a mixture of $FeCl_3$ or $FeCl_2\cdot1.5\,THF$ (6.00 mmol) and ligand (6.00 mmol) was added CH_2Cl_2 (30 mL) and the resulting solution stirred for 24 h. Filtration of the solution, followed by removal of solvent in vacuo gave a greasy solid. Washing with pentane (3 × 15 mL) gave **1** as a yellow solid (67 % yield), **2** as an orange solid (74 %), **6**, **7**, and **8** as purple solids (72, 77, and 60 %, respectively), and **9** as a dark-red solid (70 %). $[^{DIPP}(N,N)FeCl_3]$ (**3**) was prepared by heating a solution of $^{DIPP}(N,N)$ and $FeCl_3$ in THF at reflux for 18 h, followed by extraction into diethyl ether, removal of solvent, and washing with pentane to give a green-black solid (78 %).

Alkylation experiments: $[^{R}(N,N)FeCl_3]$ (0.500 mmol) was dissolved in THF (10 mL) and cooled to −78 °C followed by dropwise addition of a solution of RMgCl (0.500 mmol) in THF. An aliquot (1 mL) was removed from the reaction mixture and quenched with distilled H_2O. Subsequent aliquots were removed and quenched over a range of temperatures. Aliquots were filtered through basic alumina and analysed by GC or GC/MS. GC area counts were corrected against organic components present in unreacted RMgCl.

Polymerization experiments: Styrene (5.000 g, 48.00 mmol), 1-phenylethyl chloride (32.0 μL, 0.240 mmol), and catalyst (0.240 mmol) were added to an ampoule equipped with a magnetic stirrer bar. The vessel was then sealed and heated to 120 °C. Conversion was determined by integration of signals for monomer versus polymer backbone in the ^1H NMR spectrum of crude aliquots (0.1 mL) removed from the reaction mixture at appropriate intervals. Upon completion of the reaction, the vessel contents were dissolved in THF and added dropwise to acidified methanol to precipitate the poly(styrene), which was washed and dried in vacuo. Samples were analysed by gel permeation chromatography against styrene standards to determine the molecular weight.

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