Supporting Information

Iron(II) β-ketiminate complexes as mediators of controlled radical polymerisation

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<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>Conv. (%)</th>
<th>$M_{n,th}$ (Da)</th>
<th>$M_n$ (Da)</th>
<th>$\mathcal{D}$</th>
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$^a$ Conditions: [styrene]:[Fe$^{II}$]:[1-PECl] = 100:1.00:1.00, styrene:toluene = 1:1 (v/v), 120$^\circ$C, 1 hour. Conversion determined by $^1$H NMR spectroscopy. $M_{n,th} = [\text{styrene}]_0/[\text{1-PECl}]_0 \times M(\text{styrene}) \times \text{conversion}.$

### Table S2 ATRP of MMA$^a$

<table>
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<tr>
<th>Entry</th>
<th>Complex</th>
<th>Conv. (%)</th>
<th>$M_{n,th}$ (Da)</th>
<th>$M_n$ (Da)</th>
<th>$\mathcal{D}$</th>
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$^a$ Conditions: [MMA]:[Fe$^{II}$]:[1-PECl] = 100:1.00:1.00, MMA:toluene = 1:1 (v/v), 120$^\circ$C, 1 hour. Conversion determined by $^1$H NMR spectroscopy. $M_{n,th} = [\text{MMA}]_0/[\text{1-PECl}]_0 \times M(\text{MMA}) \times \text{conversion}.$
Table S3 OMRP of styrene\textsuperscript{a}

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<th>Conv. (%)</th>
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<th>( M_{n,\text{th}} [\text{Fe}] ) (Da)</th>
<th>( M_n ) (Da)</th>
<th>( \bar{D} )</th>
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\( \text{Conditions: } [\text{styrene}]:[\text{Fe}^{II}]:[\text{AIBN}] = 100:1.00:1.00, \text{ styrene:toluene = 1:1 (v/v), 110°C, 1 hour. Conversion determined by } ^1H \text{ NMR spectroscopy. } M_{n,\text{th}}[\text{AIBN}] = [\text{styrene}]_0/(2 \times [\text{AIBN}]_0) \times M(\text{styrene}) \times \text{conversion. } M_{n,\text{th}}[\text{Fe}] = [\text{styrene}]_0/[\text{Fe}] \times M(\text{styrene}) \times \text{conversion.} \)

Table S4 OMRP of MMA\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>Conv. (%)</th>
<th>( M_{n,\text{th}} [\text{AIBN}] ) (Da)</th>
<th>( M_{n,\text{th}} [\text{Fe}] ) (Da)</th>
<th>( M_n ) (Da)</th>
<th>( \bar{D} )</th>
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\( \text{Conditions: } [\text{MMA}]:[\text{Fe}^{II}]:[\text{AIBN}] = 100:1.00:1.00, \text{ MMA:toluene = 1:1 (v/v), 110°C, 1 hour. Conversion determined by } ^1H \text{ NMR spectroscopy. } M_{n,\text{th}}[\text{AIBN}] = [\text{MMA}]_0/(2 \times [\text{AIBN}]_0) \times M(\text{MMA}) \times \text{conversion. } M_{n,\text{th}}[\text{Fe}] = [\text{MMA}]_0/[\text{Fe}] \times M(\text{MMA}) \times \text{conversion.} \) \( b \) Too little polymer obtained for GPC analysis.
**KINETIC DATA**

Figure S1 First-order kinetic plot for the OMRP of MMA mediated by complex 1a.

\[ \ln([M]/[M]_0) = k_{obs} t \]

\[ k_{obs} = 0.0017 \text{ s}^{-1} \]

\[ R^2 = 0.9931 \]

Conditions: [MMA]:[1a]:[AIBN] = 100:1.00:1.00, MMA:toluene = 1:1 (v/v), 110°C. Conversion determined by \(^1\)H NMR spectroscopy.

**NMR SPECTRA**

Figure S2 \(^1\)H NMR spectrum of complex 1a (500 MHz, C\(_6\)D\(_6\)).
Figure S3 $^1$H NMR spectrum of complex 2a (500 MHz, C$_6$D$_6$)

Figure S4 $^1$H NMR spectrum of complex 3a (500 MHz, THF-d$_8$)
Figure S5 $^1$H NMR spectrum of complex 4a (500 MHz, C$_6$D$_6$)

Note. The number of resonances observed in the $^1$H NMR spectrum of 1b is double what would be expected based on the solid state structure. It is possible that multiple spectroscopically distinct species (e.g. monomers, dimers, etc.) are present in solution, thus giving rise to the higher than expected number of resonances. Combustion analysis and solution magnetic moment data together confirm the expected empirical formula of this complex.
**Figure S7** $^1$H NMR spectrum of complex 1c (500 MHz, THF-d$_8$)

Note. A number of resonances corresponding to residual solvent (toluene and n-hexane) are apparent in the above spectrum, despite the spectrum being obtained from a ‘dry’ crystalline sample of complex 1c. The appearance of residual solvent presumably arises through release of crystal lattice solvent on dissolution in THF-d$_8$ (see Figure S15 for x-ray structure).

**Figure S8** $^1$H NMR spectrum of complex 3c (500 MHz, THF-d$_8$)

Note. A number of resonances corresponding to residual solvent (toluene and n-hexane) are apparent in the above spectrum, despite the spectrum being obtained from a ‘dry’ crystalline sample of complex 3c. The appearance of residual solvent presumably arises through release of crystal lattice solvent on dissolution in THF-d$_8$ (see Figure S16 for x-ray structure).
**X-RAY CRYSTALLOGRAPHIC DATA**

*Figure S9 Complex 1a*

![Diagram of complex 1a](image)

- **CCDC Code**: 1470307
- **Formula**: $C_{15}H_{35}FeN_3OSi_2$
- **Formula weight**: 385.49
- **Size**: 0.3657 x 0.2421 x 0.125 mm
- **Crystal morphology**: Green block
- **Temperature**: 119.97(18) K
- **Wavelength**: 0.71073 Å [Mo-Kα]
- **Crystal system**: Monoclinic
- **Space group**: $P2_1/c$
- **Unit cell dimensions**:
  - $a = 10.3546(6)$ Å \hspace{1cm} $\alpha = 90^\circ$
  - $b = 15.0837(4)$ Å \hspace{1cm} $\beta = 127.970(9)^\circ$
  - $c = 17.2714(10)$ Å \hspace{1cm} $\gamma = 90^\circ$
- **Volume**: 2126.6(3) Å³
- **Z**: 4
- **Density (calculated)**: 1.204 Mg/m³
- **Absorption coefficient**: 0.827 mm⁻¹
- **$F(000)$**: 832
- **Data collection range**: $2.837 \leq \Theta \leq 31.076^\circ$
- **Index ranges**: $-14 \leq h \leq 14, -21 \leq k \leq 21, -24 \leq l \leq 23$
- **Reflections collected**: 44800
- **Independent reflections**: 6463 [R(int) = 0.0539]
- **Observed reflections**: 5349 [I > 2σ(I)]
- **Absorption correction**: Gaussian
- **Max. and min. transmission**: 0.975 and 0.95
Refinement method: Full
Data / restraints / parameters: 6463 / 0 / 209
Goodness of fit: 1.055
Final $R$ indices [$I > 2\sigma(I)$]: $R_1 = 0.0393$, $wR_2 = 0.0773$
$R$ indices (all data): $R_1 = 0.0537$, $wR_2 = 0.0826$
Largest diff. peak and hole: 0.4 and -0.261 eÅ$^3$

**Figure S10** Complex 2a

CCDC Code: 1470308
Formula: C$_{16}$H$_{34}$FeN$_{2}$O$_{2}$Si$_{2}$
Formula weight: 398.48
Size: 0.5458 x 0.4191 x 0.1544 mm
Crystal morphology: Green plate
Temperature: 120.00(10) K
Wavelength: 0.71073 Å [Mo-K$_\alpha$]
Crystal system: Monoclinic
Space group: P2$_1$/c
Unit cell dimensions:
- $a = 12.06239(9)$ Å, $\alpha = 90^\circ$
- $b = 9.46682(8)$ Å, $\beta = 91.0690(7)^\circ$
- $c = 18.89946(16)$ Å, $\gamma = 90^\circ$
Volume: 2157.80(3) Å$^3$
$Z$: 4
Density (calculated): 1.227 Mg/m$^3$
Absorption coefficient: 0.819 mm$^{-1}$
$F(000)$ 856

Data collection range $2.735 \leq \theta \leq 31.12^\circ$

Index ranges $-17 \leq h \leq 17, -13 \leq k \leq 13, -26 \leq l \leq 27$

Reflections collected 44886

Independent reflections 6597 [$R(int) = 0.0339$]

Observed reflections 5798 [$I > 2\sigma(I)$]

Absorption correction Gaussian

Max. and min. transmission 0.878 and 0.702

Refinement method Full

Data / restraints / parameters 6597 / 0 / 216

Goodness of fit 1.074

Final $R$ indices [$I > 2\sigma(I)$] $R_1 = 0.0282, wR_2 = 0.0661$

$R$ indices (all data) $R_1 = 0.035, wR_2 = 0.0697$

Largest diff. peak and hole 0.366 and -0.232e.Å$^{-3}$

Figure S11 Complex 3a

CCDC Code 1470309
Formula $C_{17}H_{31}FeN_3OSi_2$
Formula weight 405.48
Size $0.4586 \times 0.1651 \times 0.109$ mm

Crystal morphology Intense green plate

Temperature 120.01(10) K

Wavelength 0.71073 Å [Mo-Kα]

Crystal system Monoclinic
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<th>Value</th>
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<td></td>
<td>(b = 16.3660(5) , \text{Å} \quad \beta = 103.421(3)^\circ)</td>
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<td></td>
<td>(c = 8.6899(3) , \text{Å} \quad \gamma = 90^\circ)</td>
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<td>(Z)</td>
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<td>Density (calculated)</td>
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<td>Absorption coefficient</td>
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<td>(F(000))</td>
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<td>0.977 and 0.905</td>
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<td>Refinement method</td>
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<td>Goodness of fit</td>
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<tr>
<td>Final (R) indices ([\text{I} &gt; 2\sigma(\text{I})])</td>
<td>(R_1 = 0.0434, , wR_2 = 0.0845)</td>
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<td>(R) indices (all data)</td>
<td>(R_1 = 0.0615, , wR_2 = 0.0915)</td>
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<td>Largest diff. peak and hole</td>
<td>0.435 and -0.311 e.Å(^3)</td>
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</table>

**Figure S12 Complex 4a**
CCDC Code 1470310
Formula $\text{C}_{18}\text{H}_{33}\text{FeN}_{3}\text{O}_{2}\text{Si}_{2}$
Formula weight 435.5
Size $0.4065 \times 0.174 \times 0.1573$ mm
Crystal morphology Green block
Temperature 120.00(10) K
Wavelength 0.71073 Å [Mo-$\text{K}_{\alpha}$]
Crystal system Triclinic
Space group $\text{P}-\text{1}$
Unit cell dimensions
\begin{align*}
a &= 8.8657(6) \text{ Å} & \alpha &= 90.425(4)^{\circ} \\
b &= 10.8724(6) \text{ Å} & \beta &= 100.153(5)^{\circ} \\
c &= 12.2568(5) \text{ Å} & \gamma &= 97.601(5)^{\circ}
\end{align*}
Volume $1152.16(11) \text{ Å}^3$
$Z$ 2
Density (calculated) 1.255 Mg/m$^3$
Absorption coefficient 0.774 mm$^{-1}$
$F(000)$ 464
Data collection range $2.814 \leq \theta \leq 31.03^{\circ}$
Index ranges $-12 \leq h \leq 11, -15 \leq k \leq 14, -17 \leq l \leq 17$
Reflections collected 24682
Independent reflections 6749 [$R(\text{int}) = 0.0535$]
Observed reflections 5501 [$I > 2\sigma(I)$]
Absorption correction Gaussian
Max. and min. transmission 0.952 and 0.905
Refinement method Full
Data / restraints / parameters 6749 / 0 / 244
Goodness of fit 1.06
Final $R$ indices [$I > 2\sigma(I)$] $R_1 = 0.0428$, $wR_2 = 0.0996$
$R$ indices (all data) $R_1 = 0.0555$, $wR_2 = 0.1088$
Largest diff. peak and hole 0.715 and -0.491 e.Å$^{-3}$
Figure S13 Complex 1b

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<td>C_{32}H_{48}Fe_{2}N_{4}O_{4}</td>
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<td>Formula weight</td>
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<td>Temperature</td>
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<td>Crystal system</td>
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<td>c = 10.7448(4) Å</td>
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<td>35409</td>
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<td>Independent reflections</td>
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<td>Observed reflections</td>
<td>4603 [I &gt;2σ(I)]</td>
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<td>Absorption correction</td>
<td>Gaussian</td>
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<tr>
<td>Max. and min. transmission</td>
<td>0.926 and 0.709</td>
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<tr>
<td>Refinement method</td>
<td>Full</td>
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Data / restraints / parameters 4970 / 0 / 194
Goodness of fit 1.086
Final R indices [I >2σ(I)]
\( R_1 = 0.0318, wR_2 = 0.0707 \)
R indices (all data)
\( R_1 = 0.0359, wR_2 = 0.0723 \)
Largest diff. peak and hole 0.494 and -0.284eÅ³

Figure S14 Complex 3b

Note. Crystals of complex 3b were generally observed to be of very poor quality. However, a suitable single crystal was eventually found and a data set obtained. The asymmetric unit of complex 3b was found to contain two crystallographically-distinct [Fe(L)OBn] units, with each representing half of a (µ²-OBn)₂ bridged dimer. The two halves of each dimer are crystallographically related through inversion. After some preliminary structural refinement, a very large residual electron density peak was observed in the vicinity of Fe2, along with further, more diffuse electron density. Therefore, the [Fe(L)OBn] unit initially containing Fe2 was modelled as being split over two positions with SOFs of 0.75 for the major component (containing Fe2A) and 0.25 for the minor component (containing Fe2B). One of the 8-ketiminate methyl groups (C23) was best modelled as being common to both disorder components. Unfortunately, the OBn group of the minor disorder component appeared disordered further, and could not be satisfactorily refined without the use of EADP constraints. Therefore, this group was refined isotropically. The disordered nature of this structure accounts for the large number of checkCIF alerts.

CCDC Code 1470324
Formula C₃₆H₄₀Fe₂N₄O₄
Formula weight 704.42
Size 0.1677 x 0.1112 x 0.0678 mm
Crystal morphology Dark red plate
Temperature 120.00(10) K
Wavelength 1.54184 Å [Cu-Kα]
Crystal system Monoclinic
Space group P2₁/c
Unit cell dimensions
\( a = 8.2528(4) \) Å \( \alpha = 90° \)
\( b = 18.5226(6) \) Å \( \beta = 119.539(7)° \)
\( c = 24.7956(13) \) Å \( \gamma = 90° \)
Volume 3297.7(3) Å³
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<td>Density (calculated)</td>
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<td>53543</td>
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<tr>
<td>Independent reflections</td>
<td>6864 ( [R(int) = 0.1062] )</td>
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<tr>
<td>Observed reflections</td>
<td>5515 ( [I &gt; 2\sigma(I)] )</td>
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<td>Absorption correction</td>
<td>multi-scan</td>
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<td>Max. and min. transmission</td>
<td>1 and 0.54604</td>
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<td>Final $R$ indices ( [I &gt; 2\sigma(I)] )</td>
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<td>$R_1 = 0.102, wR_2 = 0.1922$</td>
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<td>Largest diff. peak and hole</td>
<td>0.689 and -0.506e.Å⁻³</td>
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**Figure S15 Complex 1c**

*Note. The asymmetric unit of complex 1c was found to consist of two structurally analogous dimers (only one shown below), and two regions of co-crystallized solvent. One region could be easily modelled as a molecule of toluene with an SOF of 1. The contents of the additional solvent region were a little less clear, though could be modelled as containing either one molecule of toluene (SOF = 0.66) or one molecule of hexane (SOF = 0.33) (this explains the non-integer value in the chemical formula shown below). A number of geometric and ADP constraints/restraints were required to generate chemically sensible structures of the disordered solvent.*

![Complex 1c](image)

**CCDC Code**

1470383

**Formula**

C₆₀.₃₈H₆₉Fe₂N₄O₄
Figure S16 Complex 3c

Note. Regions of diffuse, poorly resolved electron density were observed in the crystalline lattice, but could not be modelled satisfactorily as solvent (toluene or hexane). This residual electron density was removed using the SQUEEZE routine in PLATON. In all, electron density (125 electrons) pertaining to 2.5 molecules of toluene (or hexane) per unit cell was removed. This is included in the chemical formula and as a result produces many errors in checkCIF which should be ignored.
CCDC Code 1470384
Formula $\text{C}_{62.38}\text{H}_{57}\text{Fe}_{2.38}\text{N}_{4}\text{O}_{4.38}$
Formula weight 1038.32
Size 0.3462 x 0.2548 x 0.0594 mm
Crystal morphology Orange block
Temperature 120.00(10) K
Wavelength 0.71073 Å [Mo-Kα]
Crystal system Monoclinic
Space group $P2_1/c$
Unit cell dimensions $a = 12.7953(2)$ Å $\alpha = 90^\circ$
$b = 14.0417(3)$ Å $\beta = 91.2680(17)^\circ$
$c = 30.0899(6)$ Å $\gamma = 90^\circ$
Volume 5404.83(18) Å³
$Z$ 4
Density (calculated) 1.276 Mg/m³
Absorption coefficient 0.588 mm⁻¹
$F(000)$ 2173
Data collection range $2.937 \leq \theta \leq 28.281^\circ$
Index ranges $-17 \leq h \leq 17, -18 \leq k \leq 18, -40 \leq l \leq 40$
Reflections collected 140618
Independent reflections 13322 [$R(\text{int}) = 0.0579$]
Observed reflections 11966 ($I > 2\sigma(I)$)
Absorption correction Multi-scan
Max. and min. transmission 1 and 0.89445
Refinement method Full
Data / restraints / parameters 13322 / 0 / 617
**Figure S17 Complex 3c’**

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<td>γ</td>
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<td>0.624 and -0.916e.Å³</td>
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