72%) or **5** (1.30 g, 87%). Recrystallization from hexane yielded very fine needles of both compounds.

Crystal data for **5**: $C_{84}H_{126}N_{12}OSn_4$, $M_r = 1794.73$, monoclinic, space group $P2_1/c$ (no. 14), $a = 22.911(4)$, $b = 18.441(6)$, $c = 22.250(13)$ Å, $\beta = 115.30(3)^\circ$, $V = 8499(6)$ Å^3, $F(000) = 3688$; $Z = 4$, $\rho_{calcd} = 1.40$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 14.2$ cm^{-1}, crystal dimensions $0.3 \times 0.2 \times 0.1$ mm, 12145 reflections collected for $2 < \theta < 23^\circ$, 11805 independent reflections, $R1 = 0.047$ for 8396 reflections with $I > 2\sigma(I)$, $wR2 = 0.09$ (for all data), $S = 0.989$. Data collected at $T = 173(2)$ K, Enraf Nonius CAD-4 diffractometer, absorption correction, structural solution by direct methods, full-matrix least-squares refinement on F^2 with SHELXL-93 with non-hydrogen atoms anisotropic. The asymmetric unit contains two independent molecules of the Sn_2 complex and one molecule of diethyl ether solvent. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-107662. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Kinetic Resolution of Diiron Acyl Complexes—An Approach to Asymmetric Bicyclic β-Lactams**

Scott R. Gilbertson* and Omar D. Lopez

In the last few years we have been interested in the dipolar cycloaddition of nitrones with diiron acyl complexes.[1, 2] This chemistry has been shown to be effective in the diastereo- and enantioselective addition of a variety of nitrones to mono- and disubstituted α,β-unsaturated acyl complexes. It was found that, after cycloaddition, oxidation of the resultant complex gives a thioester isoxazolidine product.[1–3] It has been shown that isoxazolidines can be converted to amino alcohols through reduction of the N–O bond.[4–6] In the case of the cycloadducts discussed below, this results in the formation of thioester derivatives of β-amino acids. Here in we show that reaction of a cyclic nitrone derived from proline proceeds with one enantiomer of the diiron complex significantly faster than with the other enantiomer. Additionally the utility of this approach is demonstrated through the synthesis of a simple carbapenem.

Reaction of complex **1** with the *Z*-nitrone **2** gave the expected isoxazolidine product, which could be oxidized to the corresponding thioester **4**. Reaction with zinc and acetic acid then yielded the β-amino β-hydroxy thioester **5**. The hope was that treatment of the thioester with mercury trifluoroacetate would result in removal of the sulfur with commensurate trapping by the amine group to give the β-lactam.[7–9] Since optically active diiron acyl complexes are accessible, this approach would potentially provide a mild route to optically active β-lactams.[2] Unfortunately the initial attempt to form the β-lactam from amino alcohol **5** resulted in less than a 15% yield of the desired product **6**. It has been reported that the cyclization to give β-lactams with groups *cis* on the adjacent carbon atoms of the four-membered ring is difficult (Scheme 1).[10]

Because of this observation, and the fact that a large number of the known β-lactam antibiotics possess the opposite stereochemistry, the dipolar cycloaddition was run on an *E*-nitrone. The stereochemistry of acyclic nitrones is typically *Z*. Consequently, it was necessary to attempt the cyclization with a cyclic nitrone. *Endo* addition of such a nitrone would give a β-amino acid with the correct stereochemistry to readily form a β-lactam. Cyclization of nitrone **7** with diiron complex **1** followed by oxidative removal of the

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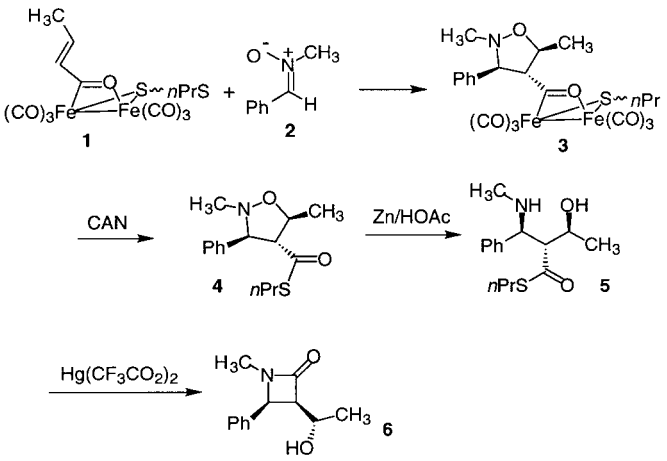
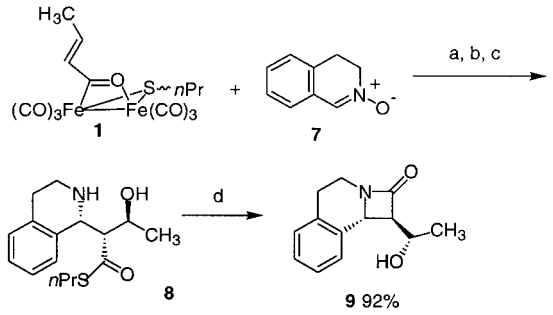


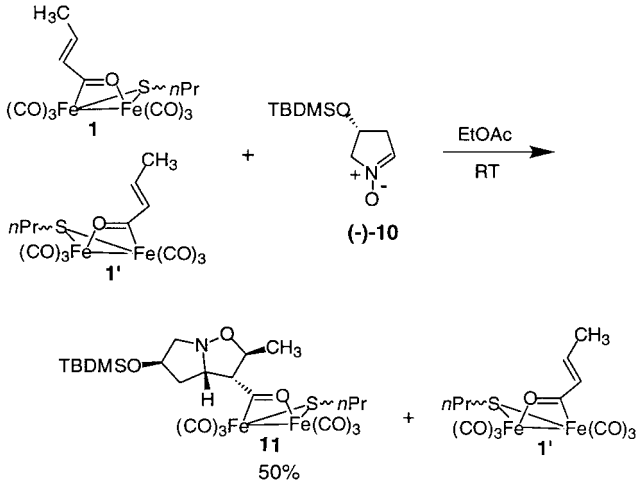
Scheme 1. Synthesis of β-lactam **6** from **1** and **2**.

metal gives the thio-ester product. Reduction of the N–O bond provides an amino thioester (**8**) that, upon treatment with mercury trifluoroacetate, readily cyclizes to the β-lactam **9**.[11] The stereochemistry obtained in this reaction not only facilitates cyclization to the β-lactam but corresponds to the stereochemistry of important carbapenems, such as thienamycin (Scheme 2).[12–17]



Scheme 2. Synthesis of **9** from **1** and **7**. a) Cycloaddition, b) CAN, CH_3CN, c) Zn, HOAc, d) $Hg(CF_3CO_2)_2$.

Once it had been established that this approach was a viable route to β-lactams, an attempt to use this reaction sequence in the synthesis of carbapenem structures was undertaken. Therefore, the racemic complex **1** was treated with enantiomerically pure nitrone **10**. This reaction resulted in a 50% yield of the expected bicyclic isoxazolidine but, surprisingly, as a single diastereomer. If both enantiomers of the racemic complex reacted with the enantiomerically pure nitrone (−)-**10**, two diastereomeric products (*S*,*S* and *S*,*R*) should have been obtained. Isolation of the unreacted starting material and measurement of its optical rotation revealed that the unreacted starting material was optically active, which confirmed that reaction with the nitrone (−)-**10** effected a kinetic resolution of the racemic complex. It was subsequently observed that, if allowed sufficient time, the other enantiomer of the iron complex also reacts with nitrone (−)-**10** (Scheme 3).

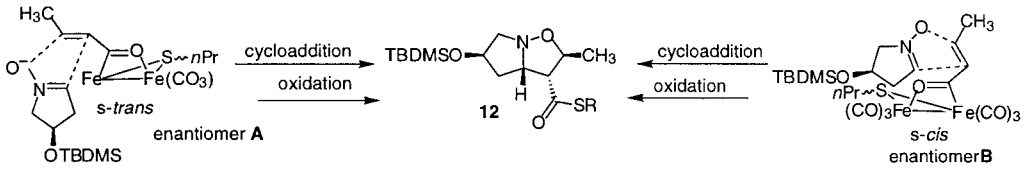


Scheme 3. Compound **11** is predominately one diastereomer, at least 20:1. The recovered starting material is highly enriched in favor of one enantiomer. TBDMS = *tert*-butyldimethylsilyl.

The selection of one enantiomer of the diiron complex by the enantiomerically pure cyclic nitrone requires consideration of a number of factors. First, the nitrone must approach the olefin from one side, most likely the side opposite the sulfur (Scheme 4). Second, given the product formed, the nitrone must react selectively through an *endo* transition state. Third, only one face of the nitrone can add to the complex; this is likely to be the face opposite the large *tert*-butyldimethylsilyl group. The last issue to consider is what conformation the complex reacts in, s-*cis* or s-*trans*. From the high selectivity, we know that either enantiomer **A** reacts in the s-*trans* conformation or enantiomer **B** reacts in the s-*cis* conformation (Scheme 4). Since we do not yet know the absolute sense of chirality of the complex at the metal center, we do not know which conformation the molecule reacts in. Given the high diastereoselectivity, we know it must be predominately one. All these issues combine to cause the enantiomerically pure nitrone to react with one of the two enantiomers of the racemic mixture with a significantly faster rate.

It is important to note that, while the stereochemistry at the metal center has not been determined, the absolute stereochemistry of the three stereogenic carbon atoms in the product is known. They have been assigned relative to the known chirality of the carbon atom which bears the hydroxy group of the nitrone. When the nitrone from *cis*-hydroxy proline ((+)-**10**), the enantiomer of (−)-**10**, is used the other enantiomer of the β-lactam is obtained.

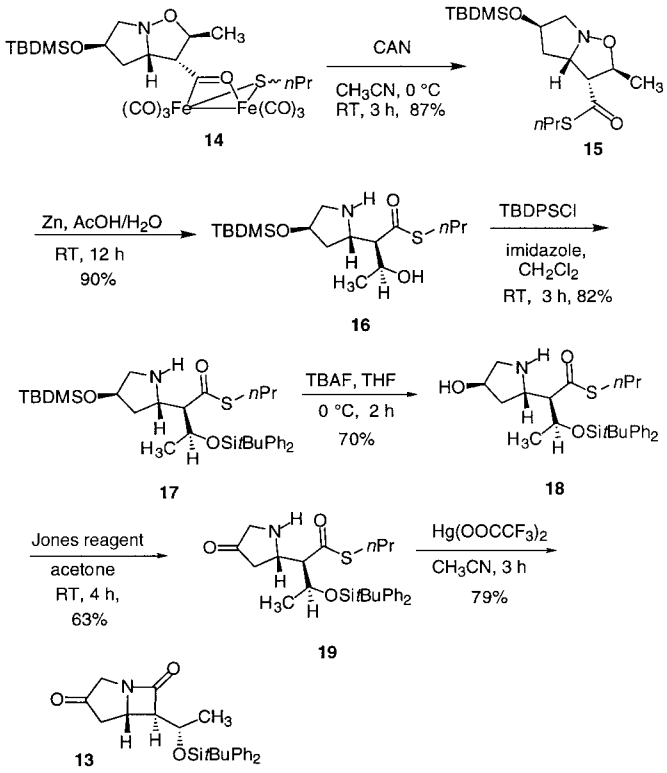
The relative rates of the reaction between a matched and mis-matched nitrone complex pair has been determined. This was done by resolution of the complex through reaction with the enantiomerically pure nitrone (−)-**10**. After resolution of



Scheme 4. The two possible *endo* transition states for product formation.

the racemic complex with nitrone (−)-**10**, the recovered, optically active starting material was then allowed to react with its matched and mismatched nitrones, (−)-**10** and its enantiomer (+)-**10**. It was observed that the complex resolved through reaction with (−)-**10** (i.e. the recovered starting material) reacted eleven times faster with nitrone (+)-**10**.

To demonstrate the potential of this approach for the synthesis of β-lactams, carbapenem **13** was synthesized (Scheme 5).[18] Cycloadduct **14** was obtained from the cyclo-



Scheme 5. Synthesis of carbapenem **13** from **14**. TBDPS = *tert*-butyldiphenylsilyl.

addition of nitrone (−)-**10** and a racemic mixture of complex **1**. The resulting complex **14** was then treated with cerium ammonium nitrate (CAN) to liberate thioester **15**. To complete the synthesis of **13**, the hydroxy group that was used to set the stereochemistry must be oxidized to a ketone. It was found that the best time for this transformation was before the β-lactam was formed. This was accomplished through reduction of the N−O bond with zinc and acetic acid, to give β-amino thioester **16**, followed by protection of the free hydroxy group as the *tert*-butyldiphenylsilyl ether (**17**). Selective removal of the *tert*-butyldimethylsilyl group with tetrabutylammonium fluoride (TBAF) then gave the desired alcohol (**18**) ready for oxidation. Jones oxidation of the free alcohol followed by cyclization with mercuric trifluoroacetate afforded optically active bicyclic β-lactam **13**. When the nitrone from *cis*-hydroxy proline ((+)-**10**) was used, the stereochemistry of the three stereogenic centers of β-lactam **13** corresponded to the stereochemistry of many therapeutically useful carbapenems, including thienamycin.

Through the reaction of nitrone (−)-**10**, optically active diiron acyl complexes can be obtained. These complexes can be used in a variety of asymmetric cycloadditions. The reaction of nitrone **10** with diiron complexes provides β-amino acids that can be converted to β-lactams with absolute stereochemistry that corresponds to the carbapenems, such as thienamycin. We are currently developing chemistry for the conversion of intermediates such as **13** into a series of biologically active β-lactams. Additionally we are attempting to determine the absolute sense of chirality of these complexes at the metal centers.

Experimental Section

General synthesis of the α,β-unsaturated acyl complexes:

A 100 mL, round-bottomed flask was charged with $[Fe_3(CO)_{12}]$ (5.00 g, 9.93 mmol) and flushed with nitrogen. THF (120 mL) was added, followed by the addition of *n*-propanethiol (0.87 g, 11.40 mmol) and triethylamine (1.17 g, 11.53 mmol). The solution was stirred for 20 min, during which time a color change of green to yellow-brown occurred. Then *trans*-crotonyl chloride (2.10 g, 20.25 mmol) was added. During this addition, gas evolution was observed. The mixture was stirred for 15 h, during which time the reaction mixture turned dark red and a white precipitate formed. The solution was filtered and the solvent removed to leave a red oil. The product was purified by silica gel chromatography (hexane) to give 3.40 g (8.02 mmol, 81 %) of a slightly air-sensitive, dark red oil. A product which corresponded to the CO deinsertion product, as described by Seyferth et al., eluted before the desired product.[3, 19–21]

Sample dipolar cycloaddition: Crotonyl acyl complex **1** (1.6 g, 3.78 mmol) was dissolved in ethyl acetate (20 mL) and transferred to a 50 mL Schlenk tube. Nitrone (−)-**10** (974.0 mg, 4.53 mmol) was added and the mixture was degassed by three freeze-pump-thaw cycles. Once degassed the reaction mixture was stirred for 3 h. The product was purified by column chromatography (silica gel, ethyl acetate/hexane 5/95) and isolated as a red oil; 1.89 mmol, 50 %. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.33$ (dd, $J = 7.8$, 7.2 Hz, 1H), 4.25 (dq, $J = 6.0$, 4.5 Hz, 1H), 3.85 (dd, $J = 9.0$, 8.1 Hz, 1H), 3.72 (m, 1H), 3.04 (dd, $J = 10.0$, 4.8 Hz, 2H), 2.81 (m, 2H), 1.86 (m, 2H), 1.53 (m, 1H), 1.38 (m, 2H), 1.13 (t, $J = 7.5$ Hz, 3H), 1.01 (d, $J = 6$ Hz, 3H), 0.87 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); minor isomer: 4.40 (m, 1H), 3.77 (m, 1H), 3.11 (t, $J = 5.9$ Hz, 1H), 2.97 (d, $J = 5.74$ Hz, 1H), 1.14 (t, $J = 7.3$ Hz, 3H), 1.00 (d, $J = 5.6$ Hz, 3H), 0.86 (s, 9H); 0.03 (s, 3H); 0.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 300.3$, 211.5, 211.2, 208.9, 208.7, 208.6, 81.4, 72.3, 72.0, 65.4, 65.0, 40.6, 37.3, 26.8, 25.8, 18.0, 17.4, 13.4, −4.7, −4.8; minor isomer: 82.4, 72.9, 72.7, 65.9, 65.3, 40.8, 36.7, 25.7, 18.1, 13.5, −4.9; IR (thin film): $\tilde{\nu} = 2932$, 2898, 2858, 2074, 2031, 1997, 1970, 1462, 1114, 1071 cm^{-1}; FAB-MS: *m/z* (%): 641 ([*M* + H, 10), 133 (100); HRFAB-MS: calcd for $C_{23}H_{34}Fe_2NO_9SSi$: *m/z*: [*M* + H] 640.0422, found 640.0413; TLC: R_f: 0.52 (ethyl acetate/hexane 15/85).

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Surface Coordination Chemistry: Corrosion Inhibition by Tetranuclear Cluster Formation of Iron with Salicylaldoxime**

Jacqueline M. Thorpe, Roy L. Beddoes, David Collison,* C. David Garner,* Madeleine Helliwell, Jeremy M. Holmes, and Peter A. Tasker

The corrosion of metals represents a waste of both natural resources and money. Corrosion can cause catastrophic accidents because of premature failure of metallic equipment. The world's supply of metals is limited, and wastage due to corrosion leads to consumption of energy and water reserves for producing and fabricating metallic structures. Acorga P5000 (referred to as P50) is a modern corrosion inhibitor for iron and comprises 5-nonylsalicylaldoxime as a mixture of carbon-chain isomers.[1] P50 was developed as an extraction agent for copper,[2] and bis-salicylaldoxime complexes of many dipositive metal ions are known.[3] However, there is no information on the mode of action of P50 on iron surfaces, and data available on iron(II) and iron(III) salicylaldoximate complexes are scant and contradictory.[4–7] We have already identified a variety of bonding modes for salicylaldoxime oligomers with vanadium and zinc.[8] When steel is treated with P50, a purple coating is formed on the surface and constitutes the protective film. Here we describe the iron chemistry of salicylaldoxime and alkyl-substituted analogues and compare the products of these reactions with corresponding materials produced by treating mild steel with these reagents.

Reaction[9] of iron(III) chloride with salicylaldoxime (H_2SalH)[8] led to crystals formulated as $[\{Fe(SalH)(HSalH)\}_4]\cdot H_2SalH\cdot 2\,C_8H_{10}$ (**1**).[10] Compound **1** comprises two molecules of xylene, a molecule of H_2SalH, and a cluster containing four Fe^{III} centers, each of which has a distorted octahedral coordination environment with four O and two *cis*-N donor atoms (Figure 1). Each Fe^{III} center is ligated by a terminal, bidentate HSalH *N*,*O*-donor ligand (those containing N1, N3, N5, and N7 function in this manner) and four atoms (1 N and 3 O) of three of the four bridging SalH ligands (those containing N2, N4, N6, and N8). Each of these bridging ligands joins two Fe^{III} centers through its oximate oxygen atom (μ-O); the attached nitrogen atom links this Fe-O-Fe moiety to a third Fe^{III} center (μ-ON), and the phenolate oxygen atom is bound to this Fe^{III} ion to form a six-membered FeNCCCO chelate ring. The structure of the cluster is further stabilized by four intramolecular hydrogen bonds between a terminal oxime NOH group of the bidentate HSalH ligand and the adjacent phenolate oxygen atom of another such ligand. A similar diversity in the bonding modes of this type of ligand occurs in $[\{VO(SalEt)(HSalEt)\}_2]$.[8]

The four Fe^{III} centers of the tetranuclear cluster of **1** have a distorted tetrahedral arrangement with Fe···Fe distances of about 3.6 Å for linkage by one μ-O and one μ-ON, and about 4.1 Å for linkage by two μ-ON groups. Tetranuclear Fe^{III} clusters, albeit with different structures, were identified in $[Fe^{III}\{Fe^{III}(salicylhydroximato)(MeOH)(acetate)\}_3]\cdot 3\,MeOH$, in which three Fe^{III} centers are arranged about a central Fe^{III} ion,[12a] and $[L_2Fe^{III}_2(\mu_3\text{-}O_2)(\mu_2\text{-}CH_3COO)_3(SalH)_2Fe^{III}_2L_2]X$ (L = 1,4,7-trimethyltriazacyclononane; X = ClO_4, PF_6), the cation of which contains a butterfly arrangement of the four Fe^{III} centers formed by two edge-sharing $Fe^{III}_3(\mu_3\text{-O})$ triangular units in which deprotonated NO groups bridge the wing and body pairs of iron atoms.[12b]

Elemental analyses, spectroscopic data, and other physical measurements[13] have demonstrated that the predominant constituent of the red-brown product obtained when an Fe salt reacts with salicylaldoxime is the tetranuclear cluster characterized in **1**. The ^{57}Fe Mössbauer isomer shift (0.53 mm s^{-1} at 77 K, 0.54 mm s^{-1} at 4.2 K) and quadrupole splitting (1.02 mm s^{-1} at 77 K, 1.05 mm s^{-1} at 4.2 K) are consistent[16–18] with a high-spin Fe^{III} system. The linewidth

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