Organometallics **2007,** *26,* 316−320

Synthesis of 1,1′-Ferrocenediyl Salicylaldimine Ligands and Their Application in Titanium-Initiated Lactide Polymerization

Robert C. J. Atkinson, Kathryn Gerry, Vernon C. Gibson,* Nicholas J. Long,*
Edward L. Marshall, and Lara J. West

Department of Chemistry, Imperial College London, London, SW7 2AZ, United Kingdom

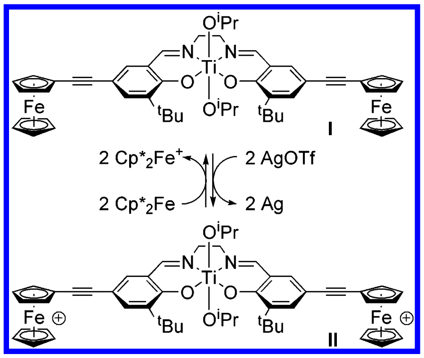
Received August 7, 2006

The synthesis of bidentate N/O 1,1′-ferrocenediyl analogues of *N*-aryl-salicylaldimines has been accomplished from the previously unreported 1′-hydroxyferrocenecarbaldehyde, **3**. Thus, the reaction of **3** with 2,6-diisopropylaniline and with aniline leads to the isolation of *N*-(2,6-diisopropylphenyl)-(1′-(hydroxy)ferrocenyl)aldimine, **5**, and *N*-phenyl-(1′-(hydroxy)ferrocenyl)aldimine, **6**, respectively. However, attempts to synthesize analogues of bis(iminophenoxide) (salen) ligands by treatment of **3** with 1,2-ethylenediamine and with *trans*-(+/−)-1,2-diaminocyclohexane led to intractable product mixtures, while reaction with 1,2-phenylenediamine resulted in formation of a substituted benzimidazole. Titanium bis(isopropoxide) complexes of **5**, **6**, and, for comparative purposes, 1′-(diphenylphosphino)hydroxyferrocene have been synthesized, and in a preliminary study all three complexes were found to initiate the ring-opening polymerization of *rac*-lactide in a well-controlled manner.

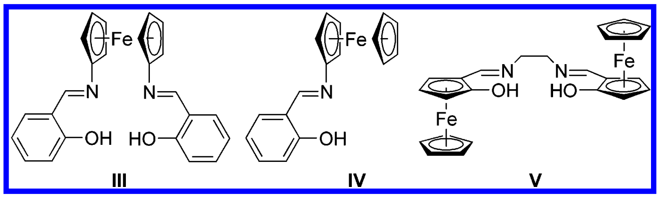
Introduction

Monoanionic, bidentate salicylaldiminates (iminophenoxides)[1] and their closely related tetradentate, dianionic relations bis(iminophenoxides) (“salen”)[2] are two of the most widely studied ligand classes in contemporary coordination chemistry, finding particularly widespread usage as supports for catalytic systems. This is in part a repercussion of their ease of synthesis (typically from inexpensive starting materials) and the simplicity with which steric and electronic properties may accordingly be varied, thereby allowing catalytic performance to be fine-tuned. As part of an ongoing research program within our laboratories, we have exploited such versatility to incorporate redox-active centers into these and other related ligand families, with the ultimate aim of synthesizing redox-switchable molecular catalysts.[3] For example, in a proof of concept study we have recently demonstrated how *rac*-lactide polymerization activity could be modulated according to the oxidation state of even remote redox centers (**I** being ca. 30 times more active than its oxidized derivative, **II**, Scheme 1).[4]

Scheme 1. Single-Site Ti-Based Lactide Polymerization Inititator Supported by a Ferrocenyl-Derivatized Salen Ligand, a Redox-Switchable Molecular Catalyst



Scheme 2. Recent Examples of “Salen”-Type Compounds with Ferrocene Units Appended



In addition, recent improvements to the synthesis of 1,1′-bis(amino)ferrocene[5] has led to its incorporation into the backbone of salen ligands (**III**, Scheme 2) and the coordination chemistry of this[3d] and substituted phenoxy analogues[6] (termed “salfen” ligands) has been described for a range of metals including Al, Mg, Ti, and Zr. Ferrocenylamine has also been employed to synthesize *N*-ferrocenylsalicylaldimine, **IV**,[7] which was shown to support moderate ethylene polymerization activity when complexed to group 4 metals.

To date, the only reported example of a salen-type ligand to be derived from a hydroxyferrocene was reported by Ito and co-workers,[8] who synthesized enantiopure 2-hydroxyferrocenecarbaldehyde via the reduction of the corresponding carboxylic

---

* Corresponding authors. E-mail: n.long@imperial.ac.uk; v.gibson@imperial.ac.uk.

(1) Calligarir, M.; Randaccio, L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D. McCleverty, J., Eds.; Pergamon Press Ltd: Oxford, 1987; Vol. 2, pp 723−726.

(2) Cozzi, P. G. *Chem. Soc. Rev.* **2004**, 410−421.

(3) (a) Gibson, V. C.; Long, N. J.; Oxford, P. J.; White, A. J. P.; Williams, D. J. *Organometallics* **2006**, *25*, 1932−1939. (b) Gibson, V. C.; Gregson, C. K. A.; Halliwell, C. M.; Long, N. J.; Oxford, P. J.; White, A. J. P.; Williams, D. J. *J. Organomet. Chem.* **2005**, *690*, 6271−6283. (c) Gibson, V. C.; Halliwell, C. M.; Long, N. J.; Oxford, P. J.; Smith, A. M.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2003**, 918−926. (d) Gibson, V. C.; Long, N. J.; Marshall, E. L.; Oxford, P. J.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2001**, 1162−1164.

(4) Gregson, C. K. A.; Gibson, V. C.; Long, N. J.; Marshall, E. L.; Oxford, P. J.; White, A. J. P. *J. Am. Chem. Soc.* **2006**, *128*, 7410−7411.

(5) Shafir, A.; Power, M. P.; Whitener, G. D.; Arnold, J. *Organometallics* **2000**, *19*, 3978−3982.

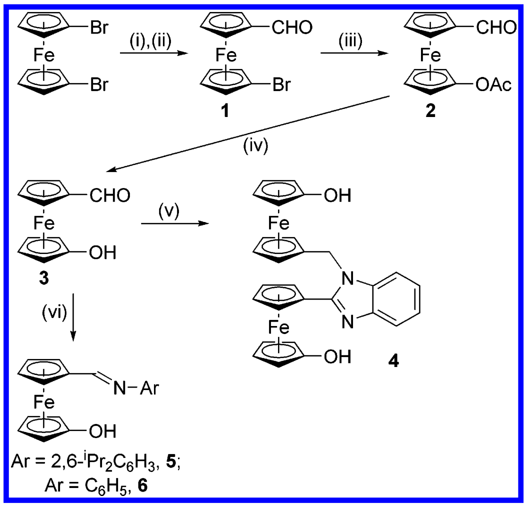
(6) Shafir, A.; Fiedler, D.; Arnold, J. *Dalton Trans.* **2002**, 555−560.

(7) Bott, R. K. J.; Schormann, M.; Hughes, D. L.; Lancaster, S. J.; Bochmann, M. *Polyhedron* **2006**, *25*, 387−396.

(8) Sawamura, M.; Sasaki, H.; Nakata, T.; Ito, Y. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2725−2729.

10.1021/om0607144 CCC: $37.00

Scheme 3. Synthesis of Compounds 3−6[a]



[a] Reagents and conditions: (i) *n*-butyllithium, THF, −78 °C, 10 min; (ii) *N*,*N*-dimethylformamide, THF, rt, 20 h; (iii) Cu_2O, acetic acid, MeCN, reflux, 15 h; (iv) 10% aq KOH, MeOH, 40 °C, 10 min; CO_2 (s); (v) 0.5 equiv of 1,2-phenylenediamine, H^+, EtOH, 80 °C, 1.5 h; (vi) **5**: 2,6-diisopropylaniline, H^+, EtOH, 80 °C, 3 h; **6**: aniline, H^+, EtOH, 80 °C, 3 h.

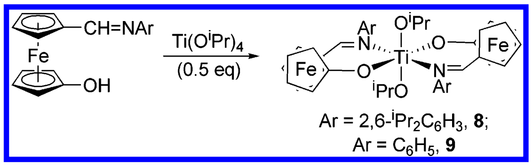
acid. Condensation with ethylenediamine gave the potentially tetradentate C_2-symmetric proligand **V**. However, this compound is extremely air and moisture sensitive and no coordination chemistry or catalysis was therefore attempted. More recently, variants of **V** featuring a carbon spacer between the cyclopentadienyl ring and the hydroxyl substituent have been reported by Bildstein and co-workers: this modification renders the ligands far more stable to air oxidation (although at the time of writing complexation studies have not been described).[9]

Prompted by the report of Bildstein,[9] here we disclose our investigations into the synthesis of ferrocenediylaldimines derived from a new 1,1′-ferrocenediyl analogue of salicylaldehyde, namely, 1′-hydroxyferrocenediylcarbaldehyde. In addition, titanium bis(isopropoxide) complexes with these proligands have been synthesized. Preliminary data concerning their ability to initiate the ring-opening polymerization of *rac*-lactide (*rac*-LA) are also presented.

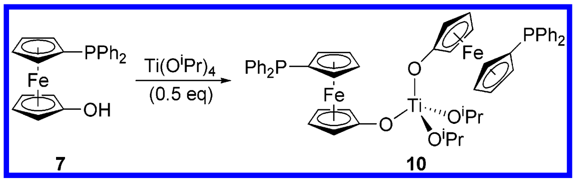
Results and Discussion

Ligand Syntheses. The synthesis of the 1,1′-ferrocenediyl analogue of salicylaldehyde, 1′-hydroxyferrocenediylcarbaldehyde, **3**, was successfully achieved via the route shown in Scheme 3. Hence, 1′-(bromo)ferrocenecarbaldehyde, **1**,[10] was refluxed with 1.3 equiv of acetic acid and 0.7 equiv of copper(I) oxide in acetonitrile for 15 h to yield **2** as a brown oil that crystallized on standing in ca. 50% yield. Hydrolysis of the acetate moiety was achieved by dissolving **2** in a 1:1 mixture of 10% aqueous potassium hydroxide solution and methanol and stirring at 40 °C for 70 min. The solution was then cooled to room temperature and solid CO_2 added slowly to lower the pH until a red precipitate was observed. This precipitate was isolated to yield **3** as a red powder in 95% yield. In common with other 1′-substituted hydroxyferrocenes,[11] **3** can be stored in air for some days with no noticeable decomposition.

Scheme 4. Synthesis of Compounds 8 and 9



Scheme 5. Synthesis of Compound 10



The ^1H NMR spectrum of **3** in CD_2Cl_2 contains four multiplets (pseudotriplets) at 3.87, 4.26, 4.66, and 4.86 ppm. A broad signal observed at 5.66 ppm arises from the OH proton (resonance sharpens in d_6-DMSO; δ 8.39), and a singlet at 9.80 ppm is attributable to the aldehydic proton. The $^{13}C\{^1H\}$ NMR spectrum features six signals arising from the cyclopentadienyl carbons and a signal at 186.4 ppm corresponding to the carbonyl carbon. The IR spectrum also exhibits diagnostic stretches at 1683 ($\nu_{C=O}$) and 3500 (ν_{O-H}) cm^{-1}.

Having successfully isolated **3**, we next attempted to convert it into salen-like proligands. However, the condensation of **3** with either 1,2-ethylenediamine or *trans*-(+/−)-1,2-diaminocyclohexane (0.5 equiv) led to intractable product mixtures (spectroscopic analysis of which provided no evidence for formation of the bis(imino alcohol)s). The analogous reaction with 1,2-phenylenediamine also failed to produce the bis(imine), instead generating the disubstituted benzimidazole **4** as an orange precipitate in 60% yield (Scheme 3). The isolation of **4** is consistent with the reported formation of *N*-ferrocenylmethyl-2-ferrocenylbenzimidazole from the reaction of ferrocenecarbaldehyde with 1,2-phenylenediamine.[12]

The synthesis of bidentate salicylaldimine ligands proceeds in a more straightforward manner. Hence, *N*-(2,6-diisopropylphenyl)-{1′-(hydroxy)ferrocenyl}aldimine, **5**, was synthesized in 85% yield by heating equimolar amounts of **3** with 2,6-diisopropylaniline in ethanol at 80°C. *N*-(Phenyl)-{1′-(hydroxy)-ferrocenyl}aldimine, **6**, was prepared in an analogous fashion (82%). Both **5** and **6** were found to be air stable and could be stored in air for several days with no noticeable decomposition.

Complexation Studies. The early transition metal coordination chemistry of **5** and **6** has been investigated by treatment with $Ti(O^iPr)_4$. For comparison, the corresponding complexation of a recently reported 1-phosphino-1′-hydroxyferrocene ligand (**7**)[11] is also described here. Thus CH_2Cl_2 solutions of **5**, **6**, or **7** (2.0 equiv) were added to $Ti(O^iPr)_4$ and stirred at room temperature overnight to afford compounds **8**, **9**, and **10**, respectively (Schemes 4 and 5).

The ^1H NMR spectrum of **8** features broad resonances consistent with a fluxional solution state structure. Nevertheless, the hydroxyferrocene aldiminate signals are clearly discernible including the ^{i}Pr methyl groups (a doublet at 1.15 ppm), the associated methine resonance (δ 3.01), and four multiplets for the ring protons (3.98, 4.27, 4.55, and 4.81 ppm). Only one imine resonance is observed (7.99 ppm), consistent with a *trans* planar or an α-*cis* ligand conformation. Although the O^{i}Pr methine resonance is obscured by the cyclopentadienyl protons, the methyl doublet is observed, overlapping with the aryl-^{i}Pr

---

(9) Wölfle, H.; Kopacka, H.; Wurst, K.; Ongania, K.-H.; Görtz, H.-H.; Preishuber-Pflügl, P.; Bildstein, B. *J. Organomet. Chem.* **2006**, *691*, 1197−1215.

(10) Dong, T. Y.; Lai, L.-L. *J. Organomet. Chem.* **1996**, *509*, 131−134.

(11) Atkinson, R. C. J.; Gibson, V. C.; Long, N. J.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2004**, 1823−1826.

(12) Benito, A.; Martinez-Manez, R.; Paya, J.; Soto, J.; Tendero, M. J. L.; Sinn, E. *J. Organomet. Chem.* **1995**, *503*, 259−263.

Table 1. Polymerization Data for the Ring-Opening of *rac*-LA Using 8−10[a]

initiator	% conversion[b] 6 h	% conversion[b] 24 h	M_n[c]	M_w/M_n[c]	P_r[d]	k_{app}/h^{-1}
8	63	96	9290	1.17	0.50	0.14
9	58	94	10 960	1.27	0.50	0.12
10	95	96	8970	1.17	0.67	0.53

[a] Toluene, 70 °C, $[LA]_0/[Ti] = 100$. [b] Determined by ^1H NMR spectroscopy ($CDCl_3$). [c] Determined by GPC ($CHCl_3$ versus polystyrene calibrants). [d] P_r = probability of racemic enchainment, determined by homonuclear decoupled ^1H NMR.

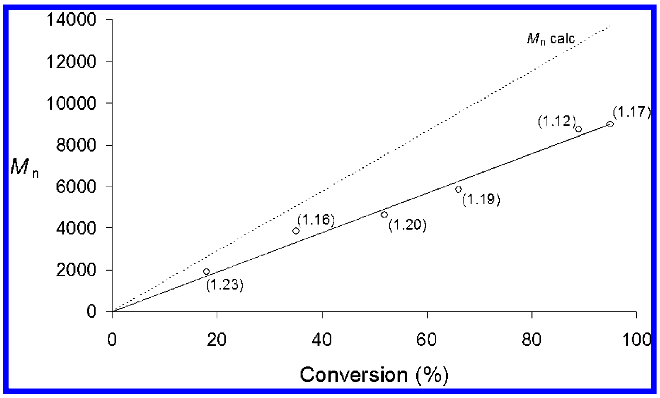


Figure 1. Plot of M_n vs monomer conversion for the polymerization of *rac*-LA using **10** (toluene, 70 °C, $[LA]_0:[\mathbf{10}] = 100$) (polydispersities shown in parentheses).

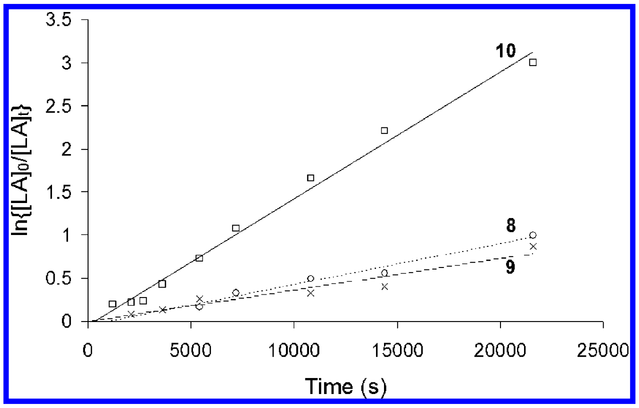


Figure 2. Plots of $\ln\{[LA]_0/[LA]t\}$ vs time for initiators **8−10** (toluene, 70 °C, $[LA]_0:[Ti] = 100$).

methyl doublet at δ 1.15. Elemental analysis results were also consistent with the proposed formulation.

The ^1H NMR spectrum of **9** is less readily assigned with even broader resonances, consistent with increased mobility due to the smaller *N*-substituent. The O^iPr methyls are observed at 1.22 ppm (the methine proton is hidden by the ferrocenyl multiplet resonances at 3.70, 4.04, 4.35, and 4.82 ppm). The presence of the isopropoxide ligands is confirmed by ^{13}C NMR (δ 25.6, $CH(CH_3)_3$; 81.5, $CHMe_2$). The imine protons give rise to a single broad signal at 8.37 ppm. Despite the overall similarity to the ^1H and ^{13}C spectra of **8**, satisfactory elemental analysis could not be obtained for this product, even after repeated attempts at purification. Although we acknowledge that the smaller steric bulk of **6** relative to **5** may lead to complications such as tris(chelation), the similar lactide polymerization behavior exhibited by both **8** and **9** (*vide infra*) is further evidence that the two titanium complexes share a common structural motif.

Finally, the titanium bis-isopropoxide complex of 1′-(diphenylphosphino)hydroxyferrocene, **7**, was also synthesized by stirring 2 equiv of the ligand with titanium(IV) isopropoxide in CH_2Cl_2 at 30 °C for 15 h to afford complex **10** as a red powder in 45% yield. ^1H NMR spectral data (in toluene-d_8) fully supports the proposed four-coordinate structure (Scheme 5) including multiplets at δ 3.67, 4.15, 4.21, and 4.35 (cyclopentadienyl protons), a septet at δ 4.57, and a doublet at δ 1.22 (both due to the isopropoxide groups). ^{31}P NMR also indicates that the phosphine units are not bound to the titanium, giving rise to a single resonance at −16.5 ppm (cf. corresponding resonance for **7** in C_6D_6: −18.0 ppm), although the possibility of hemilabile coordination in solution cannot be entirely dismissed.

Repeated attempts to gain structural information on the ligands and, more importantly, the titanium complexes unfortunately failed largely due to decomposition of the samples in solution over prolonged periods of time. We have, however, reported the structural determination of ligand **7**.[11]

Polymerization Studies. The ring-opening polymerization of *rac*-LA has been investigated using **8**, **9**, and **10** as initiators in toluene at 70 °C ($[LA]_0:[Ti] = 100$; see Table 1). All three complexes initiate well-controlled polymerizations, characterized by relatively narrow molecular weight distributions. This behavior is exemplified in Figure 1, which shows a linear increase in chain length with monomer conversion recorded with initiator **10**. Linear plots of $\ln\{[LA]_0/[LA]_t\}$ versus time (shown in Figure 2) further indicate that the polymerizations are all first-order in monomer and show that **10** is far more active than either **8** or **9**. Indeed, complex **10** required just 6 h to attain high conversion and is therefore one of the most active known titanium-based initiators for this process[4,13] (possibly a repercussion of the relatively low coordination number of the metal center in this complex). In addition, no significant induction period is observed prior to propagation for the three initiators, unlike related $(salen)Ti(O^iPr)_2$ initiators, which in some cases exhibit induction delays of up to 8 h under comparable conditions.[4]

Furthermore, initiators **8−10** differ fundamentally from their salen-supported analogues[4] by generating two polyester chains from every titanium center. Thus, M_n values reported in Table 1 are approximately half those recorded with $(salen)Ti(O^iPr)_2$ under comparable conditions (e.g., with salen = $(CH_2N{=}CH\text{-}3\text{-}^tBu\text{-}2\text{-}O\text{-}C_6H_3)_2$, M_n = 17 850 at 90% conversion).

As determined by homonuclear decoupled ^1H NMR spectroscopy, complex **10** exhibits moderate heteroselectivity ($P_r = 0.67$). Tellingly, the microstructure of the PLA samples using **8** is identical to that obtained from **9** (i.e., atactic, $P_r = P_m = 0.50$[14]), and this testifies to the isostructural nature of these two compounds. The similar chain lengths generated by these initiators further support this conclusion, with the slightly broader molecular weight distribution observed with **9** consistent with increased transesterification possibly promoted by thesmaller steric demands of its *N*-phenyl-substituted ancillary ligands.

---

(13) (a) Kim, Y.; Jnaneshwara, G. K.; Verkade, J. G. *Inorg. Chem.* **2003**, *42*, 1437−1447. (b) Kim, Y.; Verkade, J. G. *Macromol. Rapid Commun.* **2002**, *23*, 917−921. (c) Kim, Y.; Verkade, J. G. *Organometallics* **2002**, *21*, 2395−2399. (d) Russell, S. K.; Gamble, C. L.; Gibbins, K. J.; Juhl, K. C. S.; Mitchell, W. S.; Tumas, A. J.; Hofmeister, G. E. *Macromolecules* **2005**, *38*, 10336−10340. (e) Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Mahon, M. F. *Inorg. Chem.* **2006**, *45*, 2282−2287. (f) Chmura, A. J.; Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Mahon, M. F. *Dalton Trans.* **2006**, 887−889. (g) Gendler, S.; Segal, S.; Goldberg, I.; Goldschmidt, Z.; Kol, M. *Inorg. Chem.* **2006**, *45*, 4783−4790. (h) Patel, D.; Liddle, S. T.; Mungur, S. A.; Rodden, M.; Blake, A. J.; Arnold, P. L. *Chem. Commun.* **2006**, 1124−1126.

(14) P_r and P_m are the probabilities of racemic and meso dyad formation.

Conclusion

The previously unreported 1′-hydroxyferrocenecarbaldehyde, **3**, has been employed to prepare bidentate monoanionic salicyaldiminate ligands, which, when complexed to Ti(IV) centers, support well-behaved polymerization of *rac*-lactide. Further studies into the coordination behavior of these ligands and their redox chemistries are currently being pursued in our laboratories.

Experimental Section

General Procedures. All preparations were carried out using standard Schlenk techniques. All solvents were distilled over standard drying agents under nitrogen directly before use, and all reactions were carried out under an atmosphere of nitrogen. Chromatographic separations were carried out on silica gel (Kieselgel 60, 70−230 mesh) unless otherwise stated. ^{1}H NMR spectra were recorded using a Delta upgrade on a JEOL EX270 MHz spectrometer operating at 270.1 MHz (^{1}H). ^{13}C{^{1}H} NMR spectra were obtained on either a Bruker DRX-400 or AM-500 spectrometer. Chemical shifts (δ) are reported in ppm using the residual proton impurities in the NMR solvent as an internal reference. Infrared spectra were recorded as solutions in CH_2Cl_2 using a Perkin-Elmer 983 spectrometer. Mass spectra were recorded using EI or positive FAB methods, on an Autospec Q mass spectrometer. GPC measurements were performed in HPLC grade $CHCl_3$ at 1.0 mL min^{-1} using a Polymer Laboratories LC1220 HPLC pump and a Spark Midas autosampler connected to two 5 μm columns (300 × 7.5 mm) and a Shodex RI-101 differential refractometer. The columns were calibrated with polystyrene standards ranging in molecular weight from 2.9×10^3 to 3.2×10^6 amu, and chromatograms were analyzed using Cirrus software (Polymer Laboratories) in order to establish molecular weights and polydispersities.

Synthesis of 1′-(Acetoxy)ferrocenecarbaldehyde, $(C_5H_4OCOCH_3)(C_5H_4CHO)Fe$ (2). A mixture of **1**[10] (1.00 g, 3.42 mmol), acetic acid (0.25 cm^3, 4.4 mmol, 1.3 equiv, previously dried over molecular sieves), and Cu_2O (0.34 g, 2.4 mmol, 0.7 equiv) was heated to reflux in MeCN (60 cm^3) for 15 h under nitrogen. After cooling, CH_2Cl_2 was added (100 cm^3) and the mixture was filtered. The residue was then washed with an additional 30 cm^3 CH_2Cl_2. The filtrate and washings were combined, extracted with water (70 cm^3), and dried over $MgSO_4$. The solvent was removed in vacuo, and the resultant crude oil was purified by column chromatography (silica, hexane/EtOAc, 2:1) to yield **2** as an orange oil (0.47 g, 1.7 mmol, 51%).

Anal. Calc for $C_{13}H_{12}FeO_3$: C 57.39, H 4.45. Found: C 57.41, H 4.63. ^{1}H NMR δ ($CDCl_3$) ppm: 2.13 (s, 3H, CH_3), 4.04 (t, 2H, C_5H_4), 4.57 (t, 2H, C_5H_4), 4.63 (t, 2H, C_5H_4), 4.86 (t, 2H, C_5H_4), 9.92 (s, 1H, CHO). ^{13}C{^{1}H} NMR δ ($CDCl_3$) ppm: 21.1 (CH_3), 62.1, 64.7, 70.7, 74.2, 80.4, 116.4 (C_5H_4), 168.7 (OC═CH_3), 193.3 (CHO). IR (CH_2Cl_2) ν cm^{-1}: 1722 (C═O), 1682 (C═O). *m/z*: 272 (M$^+$), 230 (M$^+$ − OAc), 202 (M$^+$ − OAc − CHO).

Synthesis of 1′-(Hydroxy)ferrocenecarbaldehyde, $(C_5H_4OH)(C_5H_4CHO)Fe$ (3). Compound **2** (0.470 g, 1.73 mmol) was dissolved in a mixture of 10% aqueous KOH (10 cm^3) and MeOH (10 cm^3) and stirred at 40 °C for 70 min. The solution was cooled, and solid CO_2 was added slowly until a red precipitate was observed. The reaction mixture was extracted with Et_2O (3 × 10 cm^3) and the organic layer separated and dried over Na_2SO_4. The solvent was then removed in vacuo to yield **3** as a red powder (0.36 g, 1.6 mmol, 95%).

Anal. Calc for $C_{11}H_{10}FeO_2$: C 57.43, H 4.38. Found: C 57.52, H 4.52. ^{1}H NMR δ (CD_2Cl_2) ppm: 3.87 (t, 2H, C_5H_4), 4.26 (t, 2H, C_5H_4), 4.66 (t, 2H, C_5H_4), 4.86 (t, 2H, C_5H_4), 5.66 (br s, 1H, OH), 9.80 (s, 1H, CHO). ^{13}C{^{1}H} NMR δ ($CDCl_3$) ppm: 58.7, 63.8, 70.9, 74.3, 79.8, 123.8 (C_5H_4), 186.4 (CHO). IR (THF) ν cm^{-1}: 3500 (OH), 1683 (C═O). *m/z*: 230 (M$^+$), 202 (M$^+$ − CHO).

Synthesis of *N*-{$(CH_2C_5H_4)Fe(C_5H_4OH)$}-2-{$(C_5H_4)Fe(C_5H_4OH)$}-$C_7H_4N_2$ (4). Compound **3** (0.57 g, 2.49 mmol) and 1,2-phenylenediamine (0.13 g, 1.24 mmol, 0.5 equiv) were dissolved in EtOH (20 cm^3), and two drops of HCO_2H were added. The mixture was stirred at 80 °C for 1.5 h, after which time an orange precipitate was visible. The solvent was removed in vacuo, and the residue was washed with cold EtOH (5 cm^3) to yield **4** as an orange solid (0.40 g, 0.75 mmol, 60%).

Anal. Calc for $C_{28}H_{24}Fe_2N_2O_2$: C 63.19, H 4.55, N 5.26. Found: C 63.27, H 4.54, N 5.17. ^{1}H NMR δ (d_8-THF) ppm: 3.66 (t, 2H, C_5H_4), 3.84 (t, 2H, C_5H_4), 3.94 (t, 2H, C_5H_4), 3.97 (t, 2H, C_5H_4), 4.09 (m, 4H, C_5H_4), 4.42 (t, 2H, C_5H_4), 4.71 (t, 2H, C_5H_4), 5.16 (s, 2H, CH_2), 7.21 (m, 2H, C_6H_4), 7.59 (m, 2H, C_6H_4), 9.60 (br s, 2H, OH). ^{13}C{^{1}H} NMR δ (d_8-THF) ppm: 43.9 (CH_2), 57.9, 62.9, 63.1, 64.3, 69.4, 70.2, 70.5, 72.3, 83.7, 122.0 (C_5H_4), 111.1, 119.3, 123.0, 124.2, 135.8, 142.6 (C_6H_4), 153.5 (CHN). IR(CH_2Cl_2) ν cm^{-1}: 3265 (br s, O−H), 1459 (C═N). *m/z*: 532 (M$^+$), 451 (M$^+$ − C_5H_4OH), 319 (M$^+$ − $FcCH_2OH$).

Synthesis of *N*-(2,6-Diisopropylphenyl)-{1′-(hydroxy)ferrocenyl}aldimine, $(C_5H_4OH)(C_5H_4CH{=}N\text{-}2,6\text{-}{}^iPr_2C_6H_3)Fe$ (5). Compound **3** (0.270 g, 1.18 mmol) and 2,6-diisopropylaniline (0.22 cm^3, 1.2 mmol) were dissolved in EtOH (10 mL), and 1 drop of HCO_2H was added. The solution was stirred at 80 °C for 3 h and then at room temperature overnight. The solvent was removed in vacuo, and the resulting solid was washed with hexane (7 cm^3) to yield **5** as a brown powder (0.390 g, 1.01 mmol, 85%).

Anal. Calc for $C_{23}H_{27}FeNO$: C 70.96, H 6.99, N 3.60. Found: C 70.98, H 7.10, N 3.57. ^{1}H NMR δ (C_6D_6) ppm: 1.22 (d, 12H, CH_3), 3.28 (t, 2H, $CHMe_2$), 4.04 (br t, 2H, C_5H_4), 4.30 (br t, 2H, C_5H_4), 4.40 (br t, 2H, C_5H_4), 4.87 (br t, 2H, C_5H_4), 6.99 (m, 1H, C_6H_3), 7.31 (m, 2H, C_6H_3), 7.89 (s, 1H, CHN). ^{13}C{^{1}H} NMR δ (C_6D_6) ppm: 23.9 (CH_3), 28.1 ($CHMe_2$), 58.5, 63.1, 70.3, 72.8 (C_5H_4), 123.5, 124.8, 138.7, 149.5 (C_6H_3), 164.8 (CHN). IR (CH_2Cl_2) ν cm^{-1}: 3575 (s, O−H), 1633 (C═N). *m/z*: 389 (M$^+$), 372 (M$^+$ − OH), 202 (M$^+$ − CH═NAr).

Synthesis of *N*-(Phenyl)-{1′-(hydroxy)ferrocenyl}aldimine, $(C_5H_4OH)(C_5H_4CH{=}NPh)Fe$ (6). Compound **3** (0.18 g, 0.78 mmol) and aniline (0.07 cm^3, 0.8 mmol) were dissolved in EtOH (10 mL), and 1 drop of HCO_2H was added. The solution was stirred at 80 °C for 3 h and then at room temperature overnight. The solvent was removed in vacuo, and the resulting solid was washed with hexane (7 cm^3) to yield **6** as a red-brown powder (0.19 g, 0.63 mmol, 82%).

Anal. Calc for $C_{17}H_{15}FeNO$: C 66.91, H 4.95, N 4.59. Found: C 66.82, H 4.95, N 4.47. ^{1}H NMR δ (d_8-THF) ppm: 3.75 (t, 2H, C_5H_4), 4.04 (t, 2H, C_5H_4), 4.38 (t, 2H, C_5H_4), 4.75 (t, 2H, C_5H_4), 7.08 (d, 3H, C_6H_5), 7.27 (t, 2H, C_6H_5), 8.28 (s, 1H, CHN). ^{13}C{^{1}H} NMR δ (d_8-THF) ppm: 58.1, 63.3, 70.4, 72.1, 82.5, 114.9 (C_5H_4), 121.4, 125.3, 129.5, 154.6 (C_6H_5), 161.6 (CHN). IR (CH_2Cl_2) ν cm^{-1}: 3570 (br s, O−H), 1624 (C═N). *m/z*: 305 (M$^+$).

Synthesis of $[(C_5H_4O)(C_5H_4CH{=}N\text{-}2,6\text{-}{}^iPr_2C_6H_3)Fe]_2Ti(O^iPr)_2$ (8). Compound **5** (0.080 g, 0.21 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and added via cannula to a solution of $Ti(O^iPr)_4$ (0.030 g, 0.10 mmol) in CH_2Cl_2 (10 cm^3). The reaction mixture was stirred at room temperature for 15 h. The resulting dark red solution was evaporated to dryness and the residue coevaporated with pentane (2 × 10 cm^3) to yield **8** as a dark red powder (0.055 g, 0.058 mmol, 58%).

Anal. Calc for $C_{52}H_{66}Fe_2N_2O_4Ti$: C 66.26, H 7.06, N 2.97. Found: C 66.23, H 6.99, N 2.95. ^{1}H NMR δ (CD_2Cl_2) ppm: 1.15 (2 × d, 36H, CH_3), 3.01 (sept, 4H, $ArCHMe_2$), 3.98 (br t, 4H, C_5H_4), 4.27 (br t, 4H, C_5H_4), 4.55 (br t, 4H, C_5H_4), 4.81 (br t, 4H, C_5H_4), 7.06 (m, 6H, C_6H_3), 7.99 (s, 2H, CHN). ^{13}C{^{1}H} NMR δ (CD_2Cl_2) ppm: 23.8, 25.9 (CH_3), 28.0, 80.2 ($CHMe_2$), 60.5, 63.5, 69.6, 73.5 (C_5H_4), 123.2, 123.9, 138.2, 150.1 (C_6H_3), 163.0 (CHN). *m/z*: 389 (L$^+$).

Synthesis of [(C_5H_4O)($C_5H_4CH{=}Ph$)Fe]$_2$Ti(O^iPr)$_2$ (9). Compound **6** (0.080 g, 0.26 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and added via cannula to a solution of Ti(O^iPr)$_4$ (0.038 g, 0.13 mmol) in CH_2Cl_2 (10 cm^3). The reaction mixture was stirred at room temperature for 15 h. The resulting dark red solution was evaporated to dryness and the residue coevaporated with pentane (2 × 10 cm^3) to yield **9** as a brown powder (0.040 g, 0.052 mmol, 40%).

^{1}H NMR δ (CD_2Cl_2) ppm: 1.22 (CH_3), 3.70 (br, 4H, C_5H_4), 4.04 (br, 4H, C_5H_4), 4.35 (br, 4H, C_5H_4), 4.82 (br, 4H, C_5H_4), 7.12 (m, 3H, C_6H_5), 7.33 (m, 2H, C_6H_5), 8.37 (s, 2H, CHN). ^{13}C{^{1}H} NMR δ (CD_2Cl_2) ppm: 25.6 (CH_3), 81.5 (CHMe$_2$), 60.6, 63.7, 70.2, 73.9 (C_5H_4), 121.0, 125.5, 129.4, 154.4 (C_6H_5), 162.0 (CHN). *m/z*: 307 (L^+).

Synthesis of [(C_5H_4O)($C_5H_4PPh_2$)Fe]$_2$Ti(O^iPr)$_2$ (10). 1′-(Diphenylphosphino)hydroxyferrocene[11] (**7**) (0.100 g, 0.26 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and added via cannula to a solution of Ti(O^iPr)$_4$ (0.037 g, 0.13 mmol) in CH_2Cl_2 (10 cm^3). The reaction mixture was stirred at 30 °C for 15 h. The resulting deep red solution was evaporated to dryness and the residue washed with pentane (20 cm^3). The mixture was filtered and the residue dried under vacuum to yield **10** as a deep red powder (0.055 g, 0.059 mmol, 45%).

Anal. Calc for $C_{50}H_{50}Fe_2O_4P_2Ti\cdot(CH_2Cl_2)_{0.75}$: C 60.95, H 5.19. Found: C 60.81, H 5.39. ^{1}H NMR δ ($C_6D_5CD_3$) ppm: 1.22 (d, 6H, $-OCH(CH_3)_2$), 3.67 (t, 2H, C_5H_4), 4.15 (t, 2H, C_5H_4), 4.21 (t, 2H, C_5H_4), 4.35 (t, 2H, C_5H_4), 4.57 (m, 1H, $-OCH(CH_3)_2$), 7.10 (m, 6H, PC_6H_5), 7.55 (m, 4H, PC_6H_5). ^{13}C{^{1}H} NMR δ (CD_2Cl_2) ppm: 25.5 (CH_3), 60.3, 63.7, 64.0, 73.0, 73.9 (C_5H_4), 128.4, 129.1, 135.0 (C_6H_5). ^{31}P{^{1}H} NMR δ ($C_6D_5CD_3$) ppm: −16.5. *m/z*: 386 (L^+).

Acknowledgment. We acknowledge financial support from the Department of Chemistry, Imperial College London.

OM0607144