DALTON
FULL PAPER

Formation of 1 : 1 complexes of ferrocene-containing salen ligands with Mg, Ti and Zr

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Condensation of 1,1′-diaminoferrocene with a range of salicylaldehydes resulted in the formation of the corresponding salen-type ligands in high yields. The ability of these compounds to serve as ligands was demonstrated by the formation of several 1 : 1 Zr and Ti complexes, one of which was structurally characterized and was found to feature a $^{t\text{-Bu}}$Salfen^{2-} ligand in a square-planar conformation. In addition, a related Schiff-base ligand was synthesized by condensing diaminoferrocene with 2,4-petanedione and a Zr complex of this ligand was isolated.

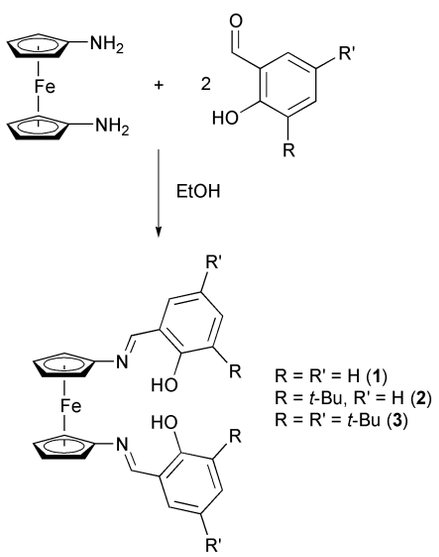
Introduction

Ferrocene-containing ligands are of widespread interest in coordination chemistry, where they are used in such diverse applications as catalysis,[1] molecular recognition and sensing.[2–5] In most of these applications, polydentate ligands are most useful due to the range of structural and electronic properties they engender on the resulting metal complexes. For example, due to the ease of acylation of ferrocene, Schiff-base ligands derived from various acyl ferrocenes provide a useful class of widely used polydentate ligands.[6–8]

We envisaged a related class of ligands with the imine nitrogen atoms attached directly to ferrocene, which we felt would lead to more electron-rich complexes that might display interesting structures and reactivity. Our recent improvement of the synthesis of 1,1′-diaminoferrocene,[9] which allows it to be prepared on useful scales in good yields, provides an excellent precursor to such ligands. Here we report the synthesis of a series of salen-like ligands incorporating a ferrocene group in the backbone. The ability of these ligands to form metal complexes was demonstrated by the synthesis and structural characterization of Group IV metal complexes.

Results and discussion

Addition of salicylaldehyde to a solution of diaminoferrocene in EtOH resulted in the immediate darkening of the reaction mixture and, after five minutes, the appearance of a burgundy-colored precipitate. The ^{1}H NMR spectrum of the compound (Salfen-H_2, **1**) is consistent with a time-averaged C_{2v} symmetry in solution, including two pseudo-triplets at 4.19 and 3.90 ppm assigned to the ferrocenyl resonances.[10] The low solubility of this compound prompted us to prepare the more soluble derivatives using 3-*tert*-butylsalicylaldehyde and 3,5-bis-*tert*-butylsalicylaldehyde (eqn. (1)).



(1)

As expected, these products ($^{t\text{-Bu}}$Salfen-H_2, **2** and $^{bis\text{-}t\text{-Bu}}$Salfen-$H_2$, **3**) were found to be soluble in low polarity solvents (Et_2O and pentane). The NMR spectra of these compounds are analogous to that of the unsubstituted **1**. All three compounds undergo reversible oxidation in THF at +10, −44 and −88 mV *vs*. Fc/Fc^+ for **1**, **2** and **3** respectively as gauged by cyclic voltammetry.

Due to the low solubility of the unsubstituted Salfen-H_2 we limited our further studies to the more soluble $^{t\text{-Bu}}$Salfen-H_2 and $^{bis\text{-}t\text{-Bu}}$Salfen-$H_2$ ligands. As part of our work on ferrocene-containing Group IV metal complexes,[11,12] **2** was reacted with $Zr(CH_2Ph)_4$ in toluene. This reaction proceeded cleanly and afforded the desired ($^{t\text{-Bu}}$Salfen)$Zr(CH_2Ph)_2$ (**4**) in 48% yield (eqn. (2)). The ^{1}H and ^{13}C NMR spectra of this complex indicate a C_{2v} symmetric structure in solution. The ferrocene resonances appear as two pseudo-triplets at 4.28 and 3.93 ppm, and the benzyl CH_2 resonance appears as a singlet at 2.52 ppm. The compound was isolated as a red crystalline solid from pentane/toluene as a solvate with one equivalent of toluene. The analogous ($^{bis\text{-}t\text{-Bu}}$Salfen)$Zr(CH_2Ph)_2$ (**5**) was prepared in a similar fashion from $^{bis\text{-}t\text{-Bu}}$Salfen-$H_2$. Its ^{1}H NMR spectrum is very similar to that of **4** and features two ferrocene pseudo-triplets at 4.33 and 3.96 ppm and a benzyl CH_2 resonance at 2.55 ppm. Attempts to reproduce these results with $Ti(CH_2Ph)_4$ led to compounds whose ^{1}H NMR spectra show a high degree of fluxionality and whose identities remain unknown.

Single crystals of ($^{t\text{-Bu}}$Salfen)$Zr(CH_2Ph)_2$ were grown from C_6D_6 and the structure of the compound, determined by X-ray crystallography, confirmed the C_{2v} symmetry in the solid state (Fig. 1 and Table 1). The crystals incorporate 1.5 equivalents of C_6D_6 per molecule of the complex. Zirconium resides in an approximate octahedral environment comprised of a square-

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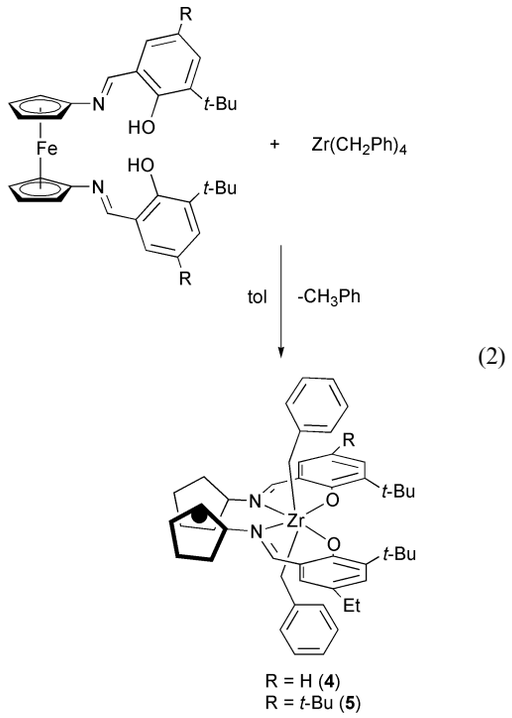


(2)

planar $^{t\text{-Bu}}$Salfen^{2-} ligand and two benzyl groups located in the axial positions. The benzylic carbons are directed away from the bulky *t*-Bu groups and towards ferrocene, with the C33–Zr–C40 angle of 142.8°. The phenyl groups, on the other hand, are pointed away from ferrocene. Ferrocene adopts an almost perfectly eclipsed conformation allowing for the two ligand arms to be in the same plane. The molecule, however, is somewhat strained as conveyed by the 3.90° tilt of the Cp rings. This tilt, coupled with the slight bending of the nitrogen atoms outwards from the plane of the Cp rings, allows for the N1 ··· N2 distance of 3.70 Å which is 0.35 Å longer than in the eclipsed

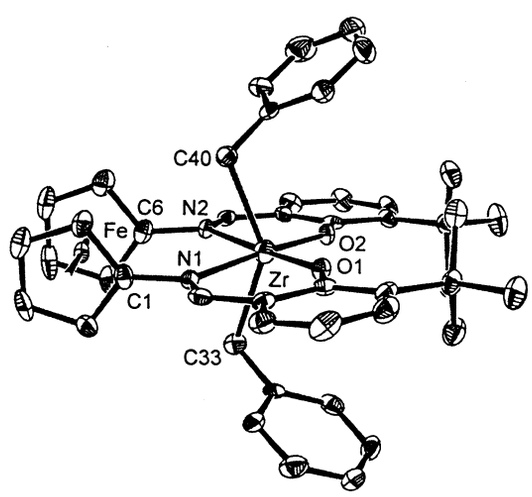


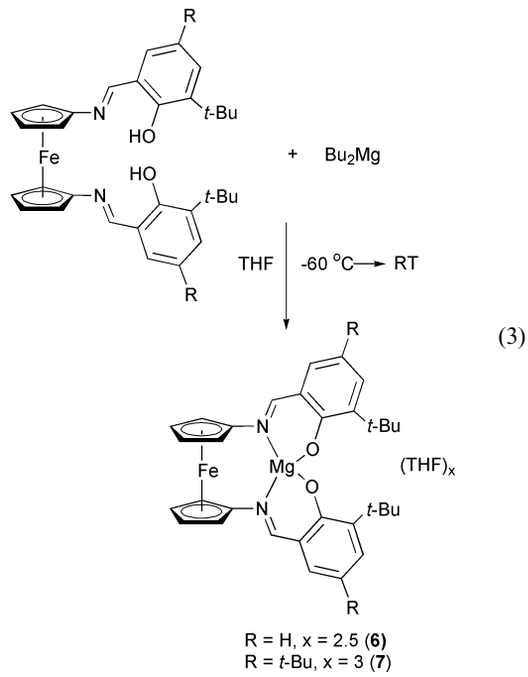
Fig. 1 An ORTEP plot of (*t*-Bu-Salfen)Zr(CH_2Ph)$_2$ drawn with 50% probability ellipsoids. All hydrogen atoms and the co-crystallized molecules of benzene are omitted for clarity.

Table 1 Selected bond lengths (Å) and angles (°) for **4**

Zr1–O1	2.013(3)	Zr1–C33	2.312(5)
Zr1–O2	2.013(3)	Zr1–C40	2.319(4)
Zr1–N1	2.356(4)	N1–C1	1.440(5)
Zr1–N2	2.361(4)	N2–C6	1.453(5)
O1–Zr1–O2	100.5(1)	N1–Zr1–O2	176.5(1)
O1–Zr1–N1	78.1(1)	C33–Zr1–C40	142.8(2)
O1–Zr1–N2	177.6(1)	Zr1–C33–C34	105.6(3)
N1–Zr1–N2	103.3(1)	Zr1–C40–C41	107.4(3)

synclinal conformation of 1,1′-diaminoferrocene.[9] The nitrogen atoms adopt a trigonal planar geometry with an average N–Zr distance of 2.36 Å and an N1–Zr–N2 bite angle of 103.3°.

Salt metathesis with metal chlorides provided an alternate route to Group IV metal complexes. To form the necessary reagents, the ligands were deprotonated by Bu_2Mg in THF affording orange solids formulated as ($^{t\text{-Bu}}$Salfen)Mg(THF)$_{2.5}$ (**6**) and ($^{\text{bis-}t\text{-Bu}}$Salfen)Mg(THF)$_3$ (**7**) (eqn. (3)). The ^{1}H NMR



(3)

spectra of these salts are consistent with a C_{2v} symmetric structure in solution. In both cases the two ferrocene resonances are almost coincidental and appear as one singlet in a spectrum recorded on a 300 MHz spectrometer. Using a higher field instrument (500 MHz) the two signals are resolved into two pseudo-triplets separated by 0.01 ppm.

The solid-state structure of **7** was determined by X-ray crystallography (Fig. 2 and Table 2). The Mg ion resides

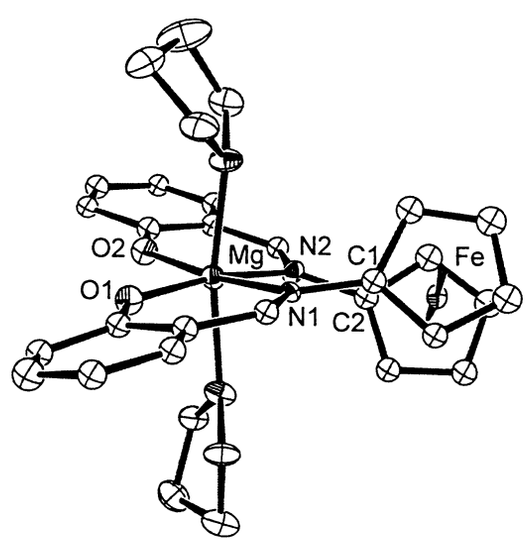


Fig. 2 An ORTEP plot of ($^{\text{bis-}t\text{-Bu}}$Salfen)Mg(THF)$_2$ molecule drawn with 50% probability ellipsoids. *t*-Bu groups and a THF of crystallization are omitted. All hydrogen atoms are also omitted for the sake of clarity.

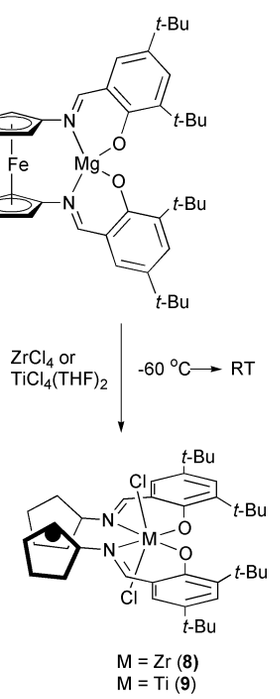
in an approximate octahedral environment composed of the $^{\text{bis-}t\text{-Bu}}$Salfen^{2-} ligand and two THF molecules. Despite the fact that the overall geometry in **7** is reminiscent of that for **4**,

Table 2 Selected bond lengths (Å) and angles (°) for **7**

Mg1–O1	1.974(5)	Mg1–O3	2.161(5)
Mg1–O2	1.984(5)	Mg1–O4	2.141(4)
Mg1–N1	2.238(6)	N1–C1	1.433(9)
Mg1–N2	2.236(7)	N2–C6	1.442(9)
O1–Mg1–O2	93.0(2)	N1–Mg1–O2	170.9(2)
O1–Mg1–N1	83.8(2)	O3–Mg1–O4	169.3(2)
O1–Mg1–N2	169.1(2)	N1–Mg1–N2	101.3

significant differences exist. Whereas in **4** the two ligand arms form a nearly perfect plane containing the Zr atom, in **7** the two ligand planes are at a 17° angle to each other. In addition, the Cp rings of the ferrocene group are in a staggered *gauche* conformation, *i.e.* rotated by approximately 36° from the fully eclipsed conformation. In addition to two coordinated THF molecules, the unit cell contains one THF of crystallization.

The ability of these magnesium complexes to undergo salt metathesis was assessed by combining **7** with $TiCl_4(THF)_2$ and $ZrCl_4$. In both cases the desired $LMCl_2$ (M = Ti, **8**; M = Zr, **9**) were obtained in high yields (eqn. (4)) and,

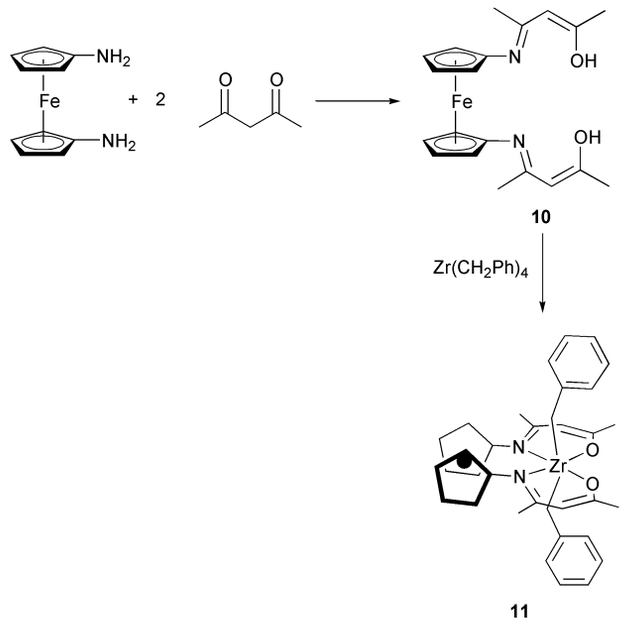


(4)

according to their NMR spectra, have structures similar to ($^{t\text{-Bu}}$Salfen)$Zr(CH_2Ph)_2$. The compounds are sparingly soluble in non-polar solvents and are quite soluble in chlorinated solvents.

In all cases, the dark-burgundy color of the Schiff-base ligands changed to yellow or red upon coordination to a metal center. We attribute these changes to the relative orientation of the N=C–Ph group with respect to the Cp π-system. In the free ligands these groups are most likely coplanar which results in an extended delocalized π-system. Complexation to a metal leads to the rotation of the N=C–Ph bond and to the disruption the π-conjugation.

Encouraged by the ease of Schiff-base condensations with diaminoferrocene, we attempted to extend this chemistry to the generation of macrocyclic compounds. *ortho*-Phenylenediamine is known to undergo a condensation with 2,4-pentanedione ("acac") in the presence of a Ni template to generate the Goedken tetrazaannulene macrocycle, which has found widespread use in transition metal chemistry.[13] However, reaction of diaminoferrocene with 2,4-pentanedione under analogous conditions resulted in the formation of another salen-like ligand Acfen-H_2 (**10**) (Scheme 1), and the same product is obtained without the use of the Ni template. It is noteworthy



Scheme 1

that, unlike the intensely colored Salfen ligands, **10** is light-yellow. We attribute this difference in part to the presence in Acfen-H_2 of methyl groups attached to the imine carbon atoms. The steric bulk of these groups prevents the ligand arms from being coplanar with the Cp rings thus disrupting the π-conjugation. The geometry of Acfen-H_2 was determined in the solid state by X-ray crystallography (Fig. 3), and the ligand

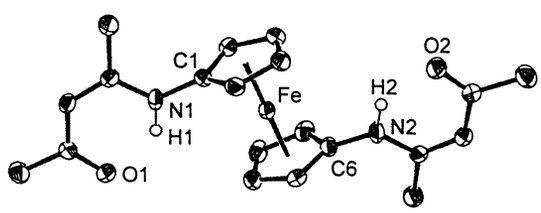


Fig. 3 An ORTEP plot of Acfen-H_2 drawn with 50% probability ellipsoids. All hydrogen atoms, except N*H*, are omitted for clarity.

arms were in fact found to be almost orthogonal to the plane of the Cp rings. The molecule adapts a staggered (antiperiplanar) conformation with the imine substituent in a *trans* orientation. Each ligand arm is held in a cisoid orientation through an intramolecular N–H ··· O hydrogen bond. We expected **10** to bind metals in a manner similar to the Salfen ligands. Indeed, reaction of Acfen-H_2 with $Zr(CH_2Ph)_4$ resulted in the formation of (Acfen)$Zr(CH_2Ph)_2$ (**11**) whose ^{1}H NMR spectrum includes two ferrocene pseudo-triplets (4.00 and 3.70 ppm), a benzylic CH_2 singlet (2.27 ppm) and a vinylic singlet (5.23 ppm) attributed to the N=C–C*H*=C proton. The compound was isolated from toluene as a yellow crystalline solid incorporating 1 equivalent of toluene.

Work in progress is aimed at uncovering the reactivity of these molecules. Details will be the focus of a separate publication.

Experimental

General considerations

Standard Schlenk-line and glove box techniques were used unless otherwise indicated. EtOH was deoxygenated by purging with N_2 gas. THF was passed through a column of activated 4Å molecular sieves and degassed with argon prior to use. All other solvents used in the preparation of metal complexes were purified by passage through a column of activated alumina and

degassed with argon prior to use. $Fc(NH_2)_2$,[9] $Zr(CH_2Ph)_4$[14] and $TiCl_4(THF)_2$ were prepared according to the literature procedures. Salicylaldehyde, 3-*tert*-butylsalicylaldehyde, 3,5-bis-*tert*-butylsalicylaldehyde, 2,4-pentanedione and Bu_2Mg were purchased from Aldrich and used as received. $TiCl_4$ and $ZrCl_4$ were purchased from Strem Chemicals. C_6D_6 was vacuum transferred from sodium/benzophenone and $CDCl_3$ was vacuum transferred from CaH_2. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at room temperature on a Bruker AM-300 or DRX-500 spectrometer. ^1H NMR chemical shifts are given relative to C_6D_5H (7.16 ppm) and $CHCl_3$ (7.26 ppm). $^{13}C\{^1H\}$ NMR spectra are relative to C_6D_6 (128.0 ppm) and $CDCl_3$ (77.2 ppm). Electrochemical measurements were performed using a BAS-100b electrochemical analyzer with a BAS C3 cell stand mounted inside an inert atmosphere glove box. The solutions studied were prepared in THF, contained 0.1 mol L^{-1} $[Bu_4N][PF_6]$ and were approximately 1 mM in analyte. Elemental analyses were determined at the Microanalytical Laboratory of the College of Chemistry, University of California, Berkeley. Single crystal X-ray structure determinations were performed at CHEXRAY, University of California, Berkeley.

Syntheses

Salfen-H_2 (1).[10] A solution of $Fc(NH_2)_2$ (1.0 g, 4.6 mmol) in 60 mL of deoxygenated absolute EtOH was treated with salicylaldehyde (0.98 mL, 9.2 mmol). The solution turned dark-red immediately and after five min a dark-burgundy precipitate formed. After 30 min of stirring the volatile fraction was removed under reduced pressure and the solid was recrystallized from a CH_2Cl_2–Et_2O mixture at −30 °C. Dark-red crystals were isolated by filtration (1.8 g, 93% yield). ^1H NMR (C_6D_6), δ 13.32 (s, 2H, OH), 8.10 (s, 2H, N=CH), 7.04–6.93 (m, 4H, ArH), 6.83 (dd, 2H, ArH), 6.59 (td, 2H, ArH), 4.19 (t, 4H, CpH), 3.90 (t, 4H, CpH) ppm. ^{13}C NMR (C_6D_6), δ 161.0 (COH), 160.5 (N=CH), 131.8 (Ar), 131.1 (Ar), 119.6 (Ar), 118.5 (Ar), 117.0 (Ar), 102.56 (Cp C–N), 68.7 (Cp), 64.0 (Cp) ppm. Mp: 197–199 °C. Anal. Calcd. for $C_{24}H_{20}N_2O_2Fe$: C, 67.94; H, 4.75; N, 6.60. Found: C, 68.09; H, 4.91; N, 6.83%.

$^{t\text{-Bu}}$Salfen-H_2 (2). A solution of $Fc(NH_2)_2$ (1.60 g, 7.40 mmol) in 40 mL of deoxygenated EtOH was treated with 3-*tert*-butylsalicylaldehyde (2.53 mL, 14.81 mmol). The dark-red reaction mixture was allowed to stir for 14 h resulting in the formation of a red-burgundy precipitate. The precipitate was collected on a fritted glass filter, washed with 2 × 5 mL of cold EtOH and dried under reduced pressure. Yield: 3.69 g, 92%. ^1H NMR (C_6D_6), δ 14.23 (s, 2H, OH), 8.19 (s, 2H, N=CH), 7.31 (d, 2H, ArH), 6.81 (d, 2H, ArH), 6.68 (t, 2H, ArH), 4.17 (t, 4H, CpH), 3.90 (t, 4H, CpH), 1.63 (s, 18H, CH_3) ppm. ^{13}C NMR (C_6D_6), δ 162.3 (COH), 161.0 (N=CH), 137.9 (Ar), 130.5 (Ar), 130.2 (Ar), 120.3 (Ar), 119.0 (Ar), 103.4 (Cp C–N), 69.6 (Cp), 65.0 (Cp), 35.5 ($C(CH_3)_3$), 30.1 ($C(CH_3)_3$) ppm. Anal. Calcd. for $C_{32}H_{36}N_2O_2Fe$: C, 71.64; H, 6.76; N, 5.22. Found: C, 71.66; H, 6.70; N, 5.22%.

$^{bis\text{-}t\text{-Bu}}$Salfen-$H_2$ (3). $Fc(NH_2)_2$ (1.38 g, 6.40 mmol) and 3,5-bis-*tert*-butylsalicylaldehyde (3.00 g, 12.8 mmol) were combined in a flask and dissolved in 80 mL of deoxygenated EtOH. The burgundy-red reaction mixture was allowed to stir for 14 h. The resulting microcrystalline solid (3.71 g, 89% yield) was isolated by filtration and washed with 2 × 20 mL of cold Et_2O. ^1H NMR (C_6D_6), δ 14.17 (s, 2H, OH), 8.36 (s, 2H, N=CH), 7.61 (d, 2H, ArH), 7.07 (d, 2H, ArH), 4.24 (t, 4H, CpH), 3.94 (t, 4H, CpH), 1.68 (s, 18H, CH_3), 1.34 (s, 18H, CH_3) ppm. ^{13}C NMR (C_6D_6), δ 161.9, 158.4, 140.2 (Ar), 137.0 (Ar), 127.0 (Ar), 126.0 (Ar), 119.0 (Ar), 103.4 (Cp C–N), 69.2 (Cp), 63.9 (Cp), 35.0 ($C(CH_3)_3$), 33.9 ($C(CH_3)_3$), 31.4 ($C(CH_3)_3$), 29.4 ($C(CH_3)_3$) ppm. Anal. Calcd. for $C_{40}H_{53}N_2O_2Fe$: C, 74.06; H, 8.08; N, 4.32. Found: C, 74.02; H, 8.44; N, 4.17%.

($^{t\text{-Bu}}$Salfen)Zr(CH_2Ph)$_2$ (4). To a cooled solution (−60 °C) of $^{t\text{-Bu}}$Salfen-H_2 (0.600 g, 1.11 mmol) in 80 mL of toluene was added a solution of $Zr(CH_2Ph)_4$ in 80 mL of toluene. The resulting dark-red solution was allowed to warm to room temperature and stirred for 12 h. The volume of the mixture was reduced to 20 mL and 10 mL of pentane was added. The mixture was cooled to −40 °C resulting in the formation of a red crystalline solid found to incorporate 1 equivalent of toluene Yield: 480 mg, 48%. ^1H NMR (C_6D_6), δ 8.03 (s, 2H, N=CH), 7.40 (dd, 2H, Ar), 7.13 (m, 2H, Ar), 7.06–7.00 (m, 3H, Ar), 6.87 (dd, 2H, Ar), 6.82 (m, 4H, Ar), 6.75–6.72 (m, 6H, Ar), 6.53 (m, 2H, Ar), 4.28 (t, 4H, CpH), 3.93 (t, 4H, CpH), 2.52 (s, 4H, benzylic CH_2), 2.11 (s, 3H, toluene CH_3), 1.54 (s, 18H, *t*-Bu CH_3) ppm. ^{13}C NMR (C_6D_6), δ 174.0, 161.9, 174.5, 139.8, 134.0, 132.7, 130.1, 126.3, 125.7, 125.3, 122.1, 119.1 (all aromatics and N=CH), 109.7 (Cp C–N), 67.6 (Cp), 67.2 (Cp), 61.2 (CH_2Ph), 35.70 ($C(CH_3)_3$), 30.87 ($C(CH_3)_3$), 21.4 (toluene). Anal. Calcd. for $C_{46}H_{48}N_2O_2FeZr\cdot C_7H_8$: C, 70.72; H, 6.27; N, 3.11. Found: C, 70.40; H, 6.59; N, 3.37%.

($^{bis\text{-}t\text{-Bu}}$Salfen)Zr($CH_2Ph$)$_2$ (5). To a cooled solution (−60 °C) of $^{bis\text{-}t\text{-Bu}}$Salfen-$H_2$ (1.28 g, 1.97 mmol) in 50 mL of toluene was added a solution of $Zr(CH_2Ph)_4$ (898 mg, 1.97 mmol) in 50 mL of toluene. The dark-red reaction mixture was allowed to warm to room temperature and stirred for 12 h. The volume was reduced and the solution was cooled to −40 °C overnight. A red, microcrystalline solid precipitate was isolated by filtration and was found to incorporate 1 equivalent of toluene. The solid was dried *in vacuo* affording 1.12 g of product (56%). ^1H NMR (C_6D_6), δ 8.10 (s, 2H, N=CH), 7.65 (d, 2H, ArH), 6.97 (d, 2H, ArH), 6.79–6.76 (m, 8H, ArH), 6.48–6.43 (m, 2H, ArH), 4.33 (t, 4H, CpH), 3.96 (t, 4H, CpH), 2.55 (s, 4H, CH_2Ph), 2.11 (s, 3H, toluene CH_3), 1.62 (s, 18H, *t*-Bu CH_3), 1.31 (s, 18H, *t*-Bu CH_3) ppm. ^{13}C NMR (C_6D_6), δ 174.2, 160.0, 147.6, 141.0, 139.0, 130.1, 129.9, 129.3, 128.3, 126.3, 125.6, 124.8 (all aromatics and N=CH), 109.7 (Cp C–N), 67.1 (Cp), 66.8 (Cp), 60.7 (CH_2Ph), 35.9 ($C(CH_3)_3$), 34.2 ($C(CH_3)_3$), 31.6 ($C(CH_3)_3$), 30.9 ($C(CH_3)_3$), 21.4 (toluene). Anal. Calcd. for $C_{54}H_{64}FeN_2O_2Zr\cdot C_7H_8$: C, 72.37; H, 7.17; N, 2.77. Found: C, 72.61; H, 7.48; N, 2.88%.

($^{t\text{-Bu}}$Salfen)Mg(THF)$_{2.5}$ (6). To a cooled solution (−60 °C) of $^{t\text{-Bu}}$Salfen-H_2 (2.50 g, 4.65 mmol) in 40 mL of THF was added a heptane solution of Bu_2Mg (1.00 M, 4.8 mL, 4.8 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 12 h. The volume of the solution was reduced to 15 mL and 50 mL of pentane was added causing an orange solid to precipitate. The flask was cooled overnight to −40 °C resulting in the formation of an orange crystalline solid which was collected and dried *in vacuo*. Yield: 2.294 g, 66%. ^1H NMR (C_6D_6), δ 8.24 (s, 2H, N=CH), 7.54 (dd, 2H, ArH), 7.04 (dd, 2H, ArH), 6.65 (t, 4H, ArH), 3.98 (m, 4H, CpH), 3.97 (m, 4H, CpH), 3.52 (m, 10H, THF), 1.84 (s, 18H, CH_3), 1.28 (m, 10H, THF). ^{13}C NMR (C_6D_6), δ 171.9, 170.2, 142.1, 134.3, 131.7, 121.4, 112.9 (all aromatics and imine N=CH), 110.1 (Cp C–N), 69.0 (CpH), 68.2 (CpH), 64.8 (THF), 35.9 ($C(CH_3)_3$), 30.2 ($C(CH_3)_3$), 25.4 (THF) ppm. Anal. Calcd. for $C_{32}H_{34}FeMgN_2O_2\cdot 2.5(C_4H_8O)$: C, 68.24; H, 7.36; N, 3.79. Found: C, 68.22; H, 7.40; N, 3.94%.

($^{bis\text{-}t\text{-Bu}}$Salfen)Mg(THF)$_3$ (7). To a cooled solution (−60 °C) of $^{bis\text{-}t\text{-Bu}}$Salfen-$H_2$ (4.35 g, 6.71 mmol) in 100 mL of THF was added a heptane solution of Bu_2Mg (1.00 M, 7.38 mL, 7.38 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 12 h. The volume of the solution was reduced to 30 mL and pentane was added causing an orange solid to precipitate. The flask was cooled overnight to −40 °C. The precipitate was isolated as an orange microcrystalline solid (4.58 g, 77% yield) and dried *in vacuo*. The product was found to incorporate 3 equivalents of THF. ^1H NMR

Table 3 Crystallographic data and refinement details for **4**, **7** and **10**

Compound	**4**·1.5(C_6H_6)	**7**	**10**
Empirical formula	$C_{55}H_{57}N_2FeO_2Zr$	$C_{52}H_{74}N_2O_5FeMg$	$C_{20}H_{24}N_2FeO_2$
M_w	935.13	887.32	380.27
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	14.2776(1)	10.2080(5)	9.5758(6)
b/Å	18.4431(3)	24.114(1)	22.837(1)
c/Å	17.6247(3)	20.3211(9)	9.6336(6)
α/°	90	90	90
β/°	95.439(1)	104.503(1)	119.290(1)
γ/°	90	90	90
V/Å^3	4620.1(1)	4842.8(3)	1837.4(2)
Z	4	4	4
T/K	152.2	137.1	162.3
μ/mm^{-1}	0.582	0.371	0.835
Refl. total	20932	18965	8945
Refl. independent	8080	7088	3378
R_{int}	0.025	0.106	0.054
Residuals: R; R_w; R_{all}	0.038; 0.050; 0.057	0.042; 0.043; 0.108	0.032, 0.034, 0.085
GOF	2.10	0.98	0.99

(C_6D_6), δ 8.31 (s, 2H, N=CH), 7.78 (d, 2H, ArH), 7.12 (d, 2H, ArH), 4.02 (m, 4H, CpH), 4.01 (m, 4H, CpH), 3.54 (m, 12H, THF), 1.91 (s, 18H, CH_3), 1.42 (s, 18H, CH_3), 1.28 (m, 12H, THF) ppm. ^{13}C NMR (C_6D_6), δ 170.6, 170.3, 141.5, 134.0, 129.7, 129.5, 120.0 (all aromatics and imine N=CH), 110.4 (Cp C–N), 68.9 (Cp), 68.1 (Cp), 64.8 (THF), 36.2 ($C(CH_3)_3$), 34.0 ($C(CH_3)_3$), 31.8 (C(CH_3)$_3$), 30.3 (*t*-Bu C(CH_3)$_3$), 25.5 (THF) ppm. Anal. Calcd. for $C_{40}H_{50}FeMgN_2O_2$·3(C_4H_8O) : C, 70.39; H, 8.41; N, 3.16. Found: C, 70.11; H, 8.61; N, 3.24%.

(bis-*t*-BuSalfen)TiCl$_2$ (8). To a cooled solution (−60 °C) of $TiCl_4(THF)_2$ (164 mg, 0.470 mmol) in 25 mL of THF was added a solution of (bis-*t*-BuSalfen)Mg(THF)$_3$ (417 mg, 0.470 mmol) in 25 ml of THF. The red solution was stirred for 2 h at −60 °C, then at room temperature for 1 h. All volatile materials were removed under reduced pressure and the resulting dark red solid was extracted with toluene and filtered. Toluene was removed *in vacuo* and the residue was washed with 10 mL of Et_2O. The product was isolated as a dark red solid (299 mg, 83%). ^{1}H NMR (C_6D_6), δ 8.46 (s, 2H, N=CH), 7.65 (d, 2H, ArH), 7.33 (d, 2H, ArH), 4.94 (t, 4H, CpH), 4.26 (t, 4H, CpH), 1.61 (s, 18H, CH_3), 1.33 (s, 18H, CH_3). ^{13}C NMR (C_6D_6), δ 169.4, 161.7, 145.3, 136.8, 130.8, 129.9, 127.1 (all aromatics and imine N=CH), 110.8 (Cp C–N), 69.3 (Cp), 66.7 (Cp), 35.8 ($C(CH_3)_3$), 34.5 ($C(CH_3)_3$), 31.3 (C(CH_3)$_3$), 30.6 (C(CH_3)$_3$). Anal. Calcd. for $C_{40}H_{50}ClFeN_2O_2Ti$: C, 62.76; H, 6.58; N, 3.66. Found: C, 62.60; H, 6.80; N, 3.55%.

(bis-*t*-BuSalfen)ZrCl$_2$ (9). To a cooled solution (−60 °C) of $ZrCl_4$ (194 mg, 0.833 mmol) in 30 mL of THF was added a solution of (bis-*t*-BuSalfen)Mg(THF)$_3$ (739 mg, 0.833 mmol) in 40 mL of THF. The red solution was allowed to warm to room temperature and was stirred for 12 h. All volatile materials were removed under reduced pressure; the red residue was extracted with toluene and filtered. Toluene was evaporated *in vacuo* and the crude product was washed with 5 mL of Et_2O. The product was isolated as a light-red microcrystalline solid (499 mg, 74%). ^{1}H NMR (C_6D_6), δ 8.24 (s, 2H, N=CH), 7.63 (d, 2H, ArH), 7.22 (d, 2H, ArH), 4.74 (t, 4H, CpH), 4.32 (t, 4H, CpH), 1.58 (s, 18H, CH_3), 1.30 (s, 18H, CH_3). ^{13}C NMR (C_6D_6), δ 173.9, 169.1, 159.0, 142.9, 138.5, 131.8, 130.3, 124.7 (Ar, N=CH), 107.3 (Cp C–N), 68.4 (Cp), 66.1 (Cp), 35.7 ($C(CH_3)_3$), 34.3 ($C(CH_3)_3$), 31.3 (C(CH_3)$_3$), 30.1 (C(CH_3)$_3$). Anal. Calcd. for $C_{40}H_{50}ClFeN_2O_2Zr$: C, 59.40; H, 6.23; N, 3.46. Found: C, 59.21; H, 6.19; N, 3.28%.

Acfen-H$_2$ (10). A solution of $Fc(NH_2)_2$ (1.50 g, 6.94 mmol) in 60 mL of deoxygenated EtOH was treated with 2,4-pentanedione (1.5 mL, 14.6 mmol). The solution was brought to reflux for 18 h. The volatile fraction was removed under reduced pressure and the resulting yellow oil was recrystallized from Et_2O at −30 °C affording a yellow crystalline product (1.65 g, 63% yield). ^{1}H NMR (C_6D_6), δ 12.54 (s, br, 2H, OH), 4.94 (s, 2H, C=CH), 4.02 (t, 4H, CpH), 3.84 (t, 4H, CpH), 2.02 (s, 6H, CH_3), 1.59 (s, 6H, CH_3) ppm. ^{13}C NMR (C_6D_6), δ 195.0, 160.5, 97.1, 95.7, 67.4 (Cp), 66.2 (Cp), 28.7 (CH_3), 18.8 (CH_3) ppm. Anal. Calcd. for $C_{20}H_{24}N_2O_2Fe$: C, 63.17; H, 6.36; N, 7.37. Found: C, 63.50; H, 6.37; N, 7.47%.

(Acfen)Zr(CH$_2$Ph)$_2$ (11). To a cooled solution (−60 °C) of Acfen-H_2 (0.500 mg, 1.32 mmol) in 40 mL of toluene was added a solution of $Zr(CH_2Ph)_4$ in 40 mL of toluene. The yellow mixture was allowed to stir for 12 h, then the solution was filtered, concentrated to 20 mL and cooled to −40 °C overnight affording 505 mg of a yellow crystalline material which was found by NMR to contain 1 equivalent of toluene. Yield: 51%. ^{1}H NMR (C_6D_6), δ 7.22–7.11 (m, 6H, Ar), 7.07–7.00 (m, 3H, Ar), 6.90–6.79 (m, 6H, Ar), 5.23 (s, 2H, C=CH), 4.00 (t, 4H, Cp), 3.70 (t, 4H, Cp), 2.27 (s, 4H, CH_2Ph), 2.11 (s, 3H, toluene CH_3), 1.73 (s, 6H, CH_3), 1.58 (s, 6H, CH_3). Anal. Calcd. for $C_{34}H_{36}FeZrN_2O_2$·C_7H_8: C, 66.20; H, 5.96; N, 3.77. Found: C, 66.42; H, 6.28; N, 3.84%.

X-Ray crystallography

Crystals of **4** suitable for X-ray diffraction were grown from C_6D_6 at room temperature. Crystals of **7** were grown by a slow diffusion of pentane into a solution of **7** in THF. Crystals of **10** were grown from Et_2O at −30 °C. A crystal of appropriate size was mounted on a glass capillary using Paratone-N hydrocarbon oil. The crystal was transferred to a Siemens SMART diffractometer/CCD area detector,[15] centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrices and cell constants were determined by collection of 60 10-s frames, followed by spot integration and least-squares refinement. An arbitrary hemisphere of data was collected, and the raw data were integrated using SAINT.[16] Cell dimensions reported were calculated from all reflections with $I > 10\sigma$. Data analysis and absorption corrections were performed using Siemens XPREP[17] and SADABS,[18] respectively. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. The structures were solved and refined with the teXsan software package,[19] and the experimental details are given in Table 3. A unit cell of (*t*-BuSalfen)Zr(CH_2Ph)$_2$ contains one molecule of C_6D_6 residing on a general position and one residing on a crystallographic

inversion center leading to the formulation of the compound as **4**·1.5(C_6H_6). A unit cell of **7** contains a cocrystallized molecule of THF in addition to the two coordinated THF molecules. In **4** and **10** all non-hydrogen atoms were refined anisotropically, however in **7** the ferrocene and phenyl carbons were refined isotropically in order to maintain a high enough data/parameter ratio. In **10** the positions of hydrogen atoms H1 and H2 (the amine nitrogens) were refined, all other hydrogens were included as fixed contributions. ORTEP diagrams were created using the ORTEP-3 software package.[20]

CCDC reference numbers 168571–168573.

See http://www.rsc.org/suppdata/dt/b1/b107066p/ for crystallographic data in CIF or other electronic format.

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