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Synthesis, Structure, and C–C Cross-Coupling Activity of (Amine)bis(phenolato)iron(acac) Complexes

Kamrul Hasan,[a] Louise N. Dawe,[b] and Christopher M. Kozak*[a]

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A series of (amine)bis(phenolato)iron(III)acac complexes has been prepared and characterized. Reaction of $Fe(acac)_3$ with the diprotonated linear tetradentate proligand *N*,*N*′-bis(4,6-di-*tert*-butyl-2-methylphenol)-*N*,*N*′-dimethyl-1,2-diaminoethane, H_2[**L1**], and tripodal tetradentate ligand precursors dimethylaminoethylamino-*N*,*N*-bis(2-methylene-4,6-di-*tert*-butylphenol), H_2[**L2**], dimethylaminoethylamino-*N*,*N*-bis(2-methylene-4-methyl-6-*tert*-butylphenol), H_2[**L3**], 2-methoxyethylamino-*N*,*N*-bis(2-methylene-4,6-di-*tert*-butylphenol), H_2[**L4**], 2-methoxyethylamino-*N*,*N*-bis(2-methylene-4-methyl-6-*tert*-butylphenol), H_2[**L5**], and 2-methoxyethylamino-*N*,*N*-bis(2-methylene-4,6-dimethylphenol), H_2[**L6**], produces the distorted octahedral Fe^{III} complexes [**L1**]Fe(acac) (**1**), [**L2**]Fe(acac) (**2**), [**L3**]Fe(acac) (**3**), [**L4**]Fe(acac) (**4**), [**L5**]Fe(acac) (**5**), and [**L6**]Fe(acac) (**6**). In all of these complexes, the phenolato oxygen atoms are *cis*-oriented. The paramagnetic Fe^{III} complexes **1**–**6** were also characterized by UV/Vis and IR spectroscopy, mass spectrometry, cyclic voltammetry, and magnetic measurements. Single crystal X-ray molecular structures have been determined for complexes **1**, **2**, **3**, **5**, and the proligand H_2[**L6**]. Preliminary investigations of complexes **1**–**6** for catalytic cross-coupling reactions of aryl Grignard reagents with cyclic and acyclic secondary alkyl halides and benzyl halides were performed. While the activity for cyclohexyl chlorides and bromides was high, cross-coupling of benzyl halides was moderate and 2-bromo- and 2-chlorobutane gave poor yields of cross-coupled product.

Introduction

The use of chelating tetradentate (amine)bis(phenolato) ligands has recently played an increasingly important role in transition-metal catalyst design. They have been predominantly used with high-oxidation-state early transition metals where they have been employed as alternative auxiliary ligands to cyclopentadienyl-based systems. In combination with group 4 and 5 metals they display high activities towards olefin or cyclic ester polymerization.[1–10] Also, group 3 and lanthanide metal complexes of these ligands have been effective as catalysts or initiators for ring-opening polymerization of lactide and ε-caprolactone.[11–16] By comparison, there has been limited use of (amine)bis(phenolato) ligands with the first row late transition metals,[17–24] whereas the chemistry of monoanionic phenoxytriamine ligands with these metals is far more developed.[25–35] We are interested in the development of new inexpensive, non-toxic, and environmentally friendly iron-based catalysts for organic synthesis. Following the pioneering work of Kochi,[36] iron catalysts have been found that are complementary to Ni or Pd systems for the coupling of Grignard reagents with organohalides.[37–40] The groups of Fürstner,[41–48] Cahiez,[49–55] Nakamura,[56–59] and others[60–64] reported various iron catalysts for cross-coupling reactions of organomagnesium halides and organohalides. Also, Bedford and coworkers showed that Fe(salen) complexes can be used as catalysts for the cross-coupling of aryl Grignard reagents with alkyl halides.[65] The use of $Fe(acac)_3$ as a source of Fe^{III} has been investigated by numerous groups because of its superior ease of handling compared to highly hygroscopic $FeCl_3$.[39,50,51,55,60,66,67] Generally, it was found that using additives such as TMEDA, NMP, or hexamethylenetetramine (HMTA) with $Fe(acac)_3$ improved selectivity for cross-coupling over homo-coupling of the Grignard reagent. Recently, we reported on Fe^{III} compounds supported by tetradentate and tridentate (amine)bis(phenolato) ligands, which are effective catalysts for cross-coupling of aryl Grignard reagents with alkyl halides, including secondary alkyl halides and benzyl halides.[68–70] We therefore began investigating whether (amine)bis(phenolato)iron(acac) complexes would be active single-component catalysts for C–C cross coupling of aryl Grignard reagents with alkyl halides. Herein we report the synthesis and structural, spectroscopic, and electrochemical characterization of a series of these complexes and preliminary studies of their C–C cross coupling activity.

[a] Centre for Green Chemistry and Catalysis, Department of Chemistry, Memorial University of Newfoundland,
St. John's, Newfoundland, A1B 3X7, Canada
Fax: +1-709-864-3702
E-mail: ckozak@mun.ca
[b] X-ray Diffraction Laboratory, Centre for Chemical Analysis, Research and Training, Memorial University of Newfoundland, St. John's, Newfoundland, A1B 3X7, Canada
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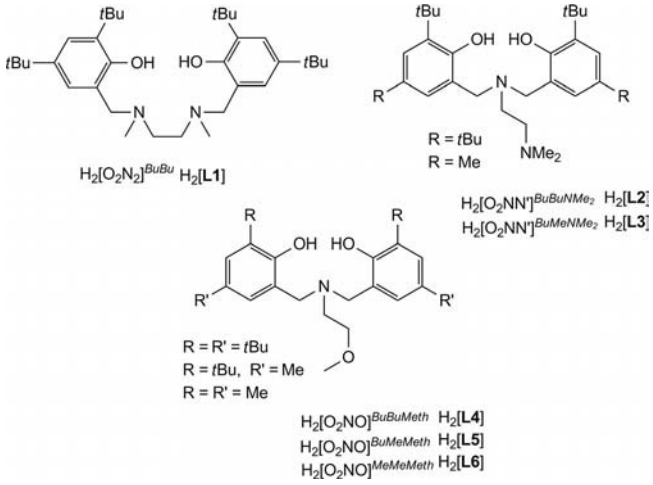
Results and Discussion

Syntheses

The substituted (amine)bis(phenolato) compounds in Scheme 1 were prepared by modified literature procedures employing Mannich condensation of the corresponding phenol, amine, and formaldehyde. Previously, these compounds have been prepared in refluxing methanol.[9,10,71–74] The use of water as a reaction medium proves much more effective at generating the desired compounds in higher yield and requires shorter heating times.[75,76] While the preparation of H_2[**L5**] by this method has previously been reported, no spectroscopic characterization was given. Therefore, we provide the synthetic procedure and characterization data for this compound here. (Amine)bis(phenolato)Fe(acac) complexes were prepared by the method reported by Bouwman,[77] who examined pyridyl-substituted (amine)bis(phenolato) complexes as catalytic driers of alkyd paints, and Chaudhuri, who performed electrochemical and magnetic studies on iron complexes of tetrahydrofurfuryl-substituted ligands.[24] Slow addition of a methanol solution of $Fe(acac)_3$ to a methanol slurry of the ligand under constant stirring, followed by addition of triethylamine gave the desired complexes (Scheme 2), which were precipitated from acetone solutions by the addition of water. The products thus obtained were generally found to be analytically pure, but in some cases contamination with unreacted proligand was observed. A detailed discussion is given below.

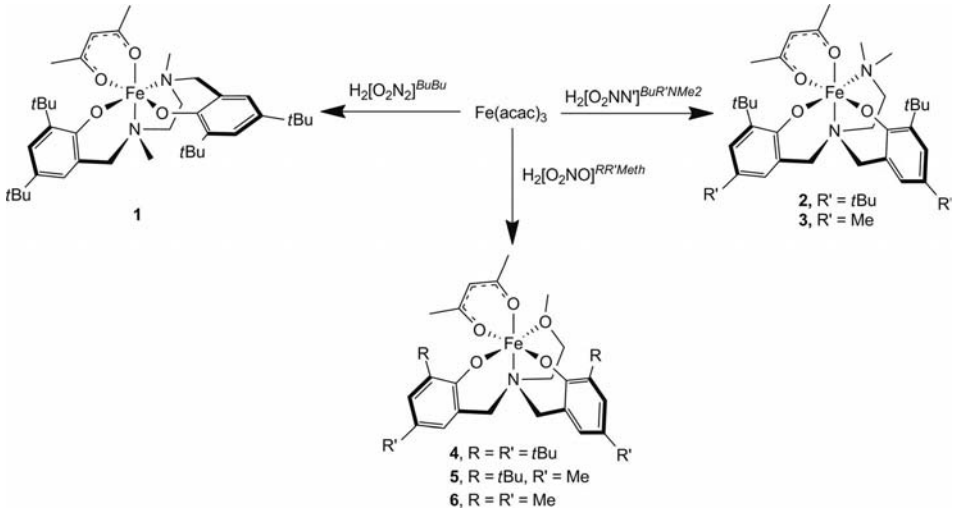


Scheme 1. (Amine)bis(phenolato) ligands used in this study.

MALDI-TOF mass spectrometry was carried out on complexes **1**–**6** using anthracene as the matrix. The mass spectra of the complexes showed molecular ion peaks and characteristic fragment ions. Namely, the acetylacetonato ligand was lost from the parent ion in all of these complexes and $[M - (acac)]^+$ peaks were observed in all spectra. IR spectra of these compounds were recorded using a diamond crystal ATR module. Most of these complexes (**1**, **2**, **3**, **4**, and **5**) show two characteristic bands at 1584 and 1520 cm^{-1} corresponding to the ν_{CO} of the acetylacetonato ligand. Complex **6** shows a band at 1570 cm^{-1} instead of 1584 cm^{-1}, possibly arising from changes in the electron density at the metal caused by varying the substituents on the phenolato groups of the ligand.

Structural Characterization

Single crystals of complexes **1**, **2**, **3**, and **5** suitable for X-ray diffraction were obtained by slow evaporation of methanol/diethyl ether (1:1) solutions. Selected bond lengths and angles are given in Table 1, and crystallographic data are given in Table 6. In all complexes the iron(III) ion is bonded to two phenolato oxygen atoms and two neutral donor atoms of the ligand. In all four complexes, the β-diketonate coligand is coordinated in the typical *cis*-fashion. The molecular structure of complex **1** is shown in Figure 1. The asymmetric unit of complex **1** contains one chiral molecule but both enantiomers are found in the unit cell. Methyl groups of the ethylenediamine fragment are *trans*-oriented. No *cis*-methyl-containing complex was present in the struc-



Scheme 2. Synthesis of (amine)bis(phenolato)iron(III)acac complexes.

Table 1. Selected bond lengths (in Å) and angles (in °) for complexes **1**, **2**, **3**, and **5**.

	1	**2**	**3**	**5**
Fe1–O1	1.900(2)	1.907(3)	1.882(4)	1.8785(11)
Fe1–O2	1.880(2)	1.899(3)	1.881(4)	1.8979(11)
Fe1–O3	2.064(3)	2.072(4)	2.066(4)	2.0722(11)
Fe1–O4	2.008(3)	1.987(4)	1.983(4)	1.9897(11)
Fe1–O5				2.2174(11)
Fe1–N1	2.234(3)	2.192(4)	2.120(6)	2.2024(13)
Fe1–N2	2.274(3)	2.290(4)	2.263(5)	
O1–C_{ipso}	1.334(4)	1.335(6)	1.331(7)	1.3333(18)
O2–C_{ipso}	1.336(4)	1.330(6)	1.327(7)	1.3380(17)
O1–Fe1–O2	97.63(11)	97.13(15)	96.00(19)	101.55(5)
O1–Fe1–O3	171.06(10)	85.48(15)	175.77(18)	88.75(5)
O1–Fe1–O4	101.53(11)	103.83(15)	93.44(18)	101.73(5)
O2–Fe1–O3	91.38(11)	177.32(15)	88.22(19)	169.41(5)
O2–Fe1–O4	91.12(11)	93.43(15)	99.38(19)	94.26(5)
O1–Fe1–N1	97.52(11)	86.60(15)	90.67(18)	89.20(5)
O2–Fe1–N1	86.36(10)	90.24(15)	84.80(18)	89.90(5)
O3–Fe1–N1	84.76(10)	89.31(15)	89.37(19)	87.77(5)
O4–Fe1–N1	167.26(11)	168.40(16)	173.79(19)	167.25(5)
N1–Fe1–N2	79.08(11)	78.70(17)	80.62(18)	
O1–Fe1–N2	87.00(10)	160.43(16)	94.57(19)	
O2–Fe1–N2	165.20(11)	95.79(15)	162.07(19)	
O3–Fe1–N2	84.94(10)	81.53(15)	81.26(19)	
O4–Fe1–N2	92.36(11)	89.97(16)	94.40(19)	
O1–Fe1–O5				161.41(5)
O2–Fe1–O5				89.35(4)
O3–Fe1–O5				80.07(5)
O4–Fe1–O5				92.31(5)
Fe1–O1–C_{ipso}	138.4(2)	131.3(3)	133.7(4)	135.42(10)
Fe1–O2–C_{ipso}	137.8(2)	133.9(3)	133.6(4)	132.63(10)

ture. Previously reported (amine)bis(phenolato)Fe^{III} halide complexes from our group using the same ligand also contained only *trans*-oriented *N*,*N*′-dimethylethylenediamine fragments.[78] However, a related structure reported by Girerd, Münck, and coworkers contains both the *trans* and *cis* isomers.[79] The geometry of the iron(III) center is distorted octahedral. The O2–Fe1–N2, O4–Fe1–N1, and O1–Fe1–O3 angles are 165.20(11)°, 167.26(11)°, and 171.06(10)°, respectively, which are less than the ideal linear geometry. The two phenolato oxygen atoms are *cis*-oriented, with O2 lying *trans* to a backbone amine donor, N2, and O1 *trans* to an oxygen atom, O3, of the acac ligand. The Fe1–O1 and Fe1–O2 distances are 1.900(2) Å and 1.880(2) Å, respectively. These bond lengths are similar to the Fe–$O_{phenolato}$ bond lengths observed in related distorted octahedral iron(III) complexes possessing phenolato ligands.[24,77,80,81] They are, however, longer than the average Fe–O bond length in trigonal bipyramidal or square pyramidal complexes, as expected because of the higher coordination number.[22,23,78,82,83] Specifically, the Fe–O distances of this complex are longer than the Fe1–O1 and Fe1–O2 distances of 1.848(2) Å and 1.862(3) Å in [**L1**]FeCl and 1.836(5) Å and 1.837(3) Å in [**L1**]FeBr employing the same (amine)bis(phenolato) ligand.[78] In complex **1**, the Fe1–N1 and Fe1–N2 bond lengths are 2.234(3) Å and 2.274(3) Å, respectively. The Fe1–N2 bond length is slightly longer than the Fe1–N1 bond length because it is *trans* to a strong phenolato oxygen donor. Typical Fe^{III}–N distances in octahedral systems are ca. 2.15–2.20 Å.[18–21,23,24,82–84] The two Fe–O bonds of the acac ligand are not identical. The Fe1–O4 bond length, which is *trans* to an amine nitrogen donor, is 2.064(3) Å whereas that of the Fe1–O3 bond *trans* to a phenolato oxygen donor is 2.008(3) Å. The lengths of O1–C1 and O2–C34 are around the average of ca. 1.33 Å found in metal complexes of (amine)bis(phenolato) ligands.[23,24,82] The Fe–O–C bond angles of complex **1** are 138.4(2)° for Fe1–O1–C1 and 137.8(2)° for Fe1–O1–C34. These bond angles are larger than those observed in previously reported (amine)bis(phenolato)Fe(acac) complexes[24,77] and suggest that the O1 and O2 atoms possess a smaller degree of sp^2 hybridization.

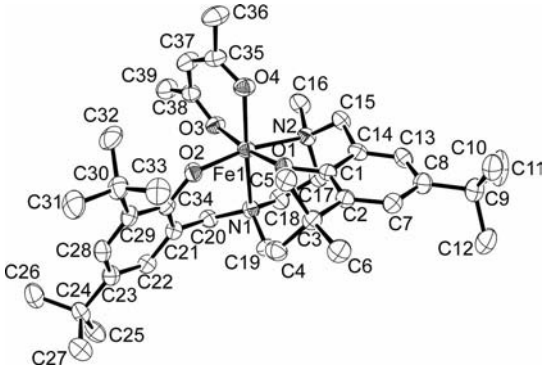


Figure 1. ORTEP diagram and atom labeling scheme for complex **1** (thermal ellipsoids shown at 50% probability). Hydrogen atoms have been removed for clarity.

The molecular structures of complexes **2** and **3** are shown in Figures 2 and 3, respectively. Both of these complexes contain two independent molecules in each asymmetric unit. Although some bond lengths and angles vary between these two molecules, metric parameters for only one of these independent molecules are presented in Table 2 for each of complexes **2** and **3**. The geometries of the Fe^{III} centers in both complexes are distorted octahedral. In complex **2**, the O1–Fe1–N2, O4–Fe1–N1, and O2–Fe1–O3 angles are 160.43(16)°, 168.40(16)°, and 177.32(15)°, respectively, which are less than the ideal linear geometry. Similarly in complex **3**, the O2–Fe1–N2, O4–Fe1–N1, and O1–Fe1–O3 angles are 162.07(19)°, 173.79(19)°, and 175.77(18)°, respectively. In complex **2**, the Fe1–O1 distance is 1.907(3) Å, and the Fe1–O2 distance is 1.899(3) Å, whereas in complex **3**, the Fe1–O1 distance is 1.882(4) Å and the Fe1–O2 distance is 1.881(4) Å. In both of these complexes, the Fe–O distances are similar to the Fe–$O_{phenolato}$ bond lengths observed in related distorted octahedral iron(III) complexes possessing phenolato ligands,[24,77,80,81] as well as those in complex **1**. The two nitrogen donor atoms in the ligand showed bond lengths of 2.192(4) Å and 2.290(4) Å for Fe1–N1 and Fe1–N2, respectively, in **2**, and lengths of 2.120(6) Å and 2.263(5) Å for Fe1–N1 and Fe1–N2, respectively, in **3**. In both complexes, the Fe1–N2 distances are longer than the Fe1–N1 distances because of the *trans*-positioned strong electron-donating phenolato oxygen. In complex **2**, the Fe1–N1 distance is similar to the previously reported Fe–N distance of (amine)bis(phenolato)Fe(acac) complexes.[24,77] However, the Fe1–N2 distance is longer than the related Fe–N distance of the octahedral complexes.[24,77,80,81] In complex **3**, the Fe1–N1 distance is shorter than the corresponding Fe–N distance of 2.181(3) Å in the previously reported trigonal bipyramidal complex, **[L3]**FeCl, employing the same ligand.[78] In complexes **2** and **3**, the Fe1–O3 distances are 2.072(4) Å and 2.066(4) Å, respectively, which are slightly longer than the Fe1–O4 distances of 1.987(4) Å and 1.983(4) Å because of their location *trans* to the phenolato oxygens. The Fe–O–C bond angles Fe1–O1–C1 [131.3(3) Å] and Fe1–O2–C34 [133.9(3) Å] in **2** and Fe1–O1–C1 [133.7(4) Å] and Fe1–O2–C28 [133.6(4) Å] in **3** are similar to the previously reported (amine)bis(phenolato)Fe^{III}acac complexes.[24,77]

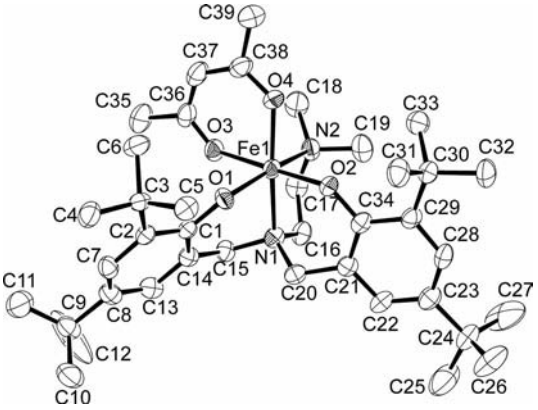


Figure 2. ORTEP diagram and atom labeling scheme for complex **2** (thermal ellipsoids shown at 50% probability). Hydrogen atoms have been removed for clarity.

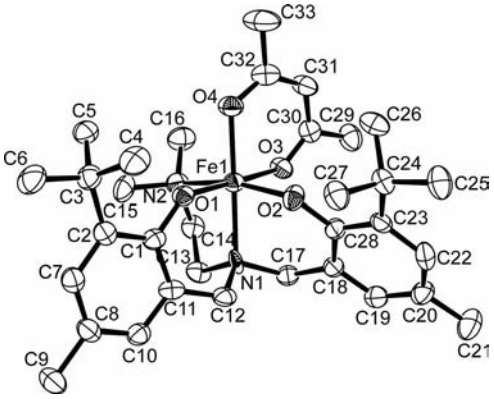


Figure 3. ORTEP diagram and atom labeling scheme for complex **3** (thermal ellipsoids shown at 50% probability). Hydrogen atoms have been removed for clarity.

Table 2. Selected bond lengths (in Å) and angles (in °) for H_2**[L6]**.

O1–C6	1.3704(17)	O1–C6–C1	121.25(13)
O2–C16	1.3752(16)	O1–C6–C5	118.14(12)
O3–C20	1.427(2)	O2–C16–C15	116.57(12)
O3–C21	1.414(2)	O2–C16–C11	122.47(12)
N4–C9	1.4684(19)	C21–O3–C20	112.50(15)
N4–C10	1.4864(18)	C10–N4–C9	109.39(11)
N4–C19	1.4730(18)	C19–N4–C9	111.76(12)

The molecular structure of complex **5** is shown in Figure 4. Unlike **2** and **3**, the asymmetric unit of complex **5** contains one molecule. The iron ion is bonded to two phenolato oxygen atoms, one neutral nitrogen donor and the oxygen of the ether pendant arm. The β-diketonate coligand is coordinated in the typical *cis*-fashion. The geometry of the iron(III) center is distorted octahedral. The two phenolato oxygen atoms are *cis*-oriented, one lying *trans* to the ether oxygen atom and the other *trans* to an oxygen atom of the acac ligand. The angles O1–Fe1–O5, O4–Fe1–N1, and O2–Fe1–O3 are 161.41(5)°, 167.25(5)°, and 169.41(5)°, respectively, which are less than a true linear geometry. The Fe1–O1 and Fe1–O2 distances are

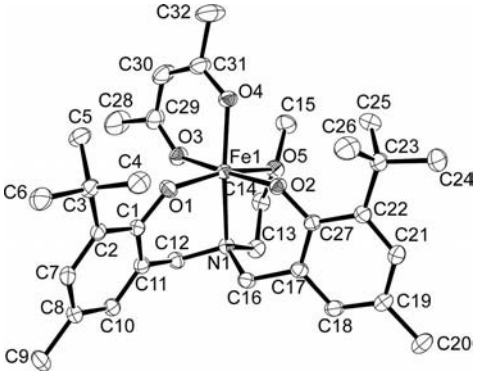


Figure 4. ORTEP diagram and atom labeling scheme for complex **5** (thermal ellipsoids shown at 50% probability). Hydrogen atoms have been removed for clarity.

1.8785(11) Å and 1.8979(11) Å, respectively, which are similar to those in complexes **1**, **2**, and **3**. The Fe1–N1 distance is 2.2024(13) Å, which is consistent with the other three complexes discussed earlier. As with complexes **1**, **2**, and **3**, the Fe1–O3 distance of 2.0722(11) Å is slightly longer than the Fe1–O4 distance of 1.9897(11) Å because of the *trans*-positioned phenolato oxygen donor. The Fe1–O1–C1 bond angle is 135.42(10)° and Fe1–O2–C27 is 132.63(10)°. The Fe1–O1–C1 angle is slightly larger than that of complexes **2** and **3** but smaller than that of complex **1**. However, the Fe1–O2–C27 angle is smaller than that of the other three complexes, **1**, **2**, and **3**.

Reaction of H_2[**L6**] with $FeCl_3$ and triethylamine afforded complex **6** as confirmed by MALDI-TOF MS and FTIR spectroscopy. However, contamination with H_2[**L6**] was evident. Recrystallization from a methanol/diethyl ether solution gave bright red-colored crystals; however, X-ray diffraction showed these crystals to be H_2[**L6**]. Because of the similar solubilities of **6** and H_2[**L6**], it was not possible to obtain pure **6** or to remove H_2[**L6**] from the product. Multiple recrystallization steps still showed contamination by H_2[**L6**]. The structure of H_2[**L6**] is shown in Figure 5. Selected bond lengths and angles are given in Table 2 and crystallographic data are given in Table 6.

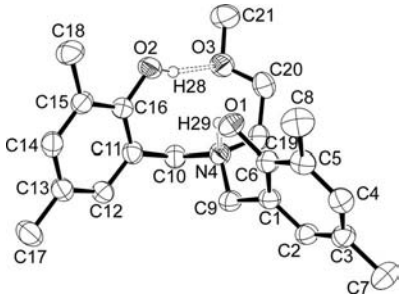


Figure 5. ORTEP diagram and atom labeling scheme for ligand H_2[**L6**] (thermal ellipsoids shown at 50% probability). Only phenol O–H hydrogen atoms are shown for clarity.

Electronic Absorption Data

Electronic absorption spectra of all the (amine)bis(phenolato)Fe(acac) complexes were recorded in methanol (Figure 6). Spectra of all the complexes show multiple intense bands in the UV and visible regions. In complexes **1**–**6**, the intense absorptions are observed in the near UV regions (below 300 nm). These are caused by $\pi \rightarrow \pi^*$ transitions involving the phenolato units and possibly the $\pi_3 \rightarrow \pi_4$ transition of the acetylacetonato (acac) ligands. Absorptions around 240 nm are observed in the spectra of unmetalated ligand precursors but the absorptions around 280 nm are also observed in (amine)bis(phenolato) complexes not containing acac ligands.[17,78,85] Two absorptions between 340–550 nm are assigned as charge-transfer transitions from the ligand-to-metal (LMCT). The high energy bands around 340 nm arise from the transitions between the p_π orbital of the phenolato oxygen and the half-filled $d_{x^2-y^2}/d_{z^2}$ orbital of high-spin Fe^{III}. The lowest energy bands around 550 nm are proposed to arise from charge transfer transitions from the p_π orbital of the phenolate to the half-filled d_{π^*} orbital of high-spin Fe^{III}. Another band around 355 nm occurs for the metal-to-ligand transition of the metal d_{xz} or d_{yz} orbital to the β-diketonate π_4 orbital, in agreement with the assignment of bands in the spectrum observed for $Fe(acac)_3$.[86,87] However, this band can overlap with the bands arising from phenolato oxygen-to-metal transitions in complexes **1**–**6**.

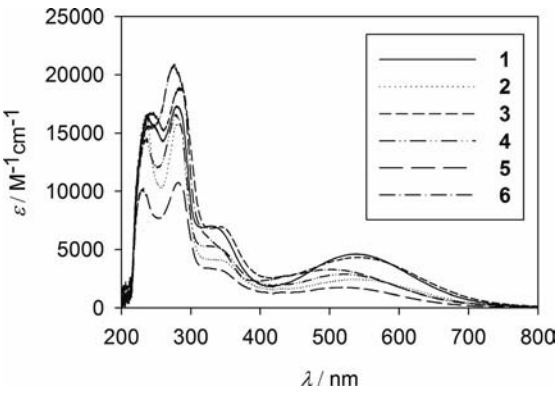


Figure 6. Electronic absorption spectra of complexes **1**–**6** in methanol.

Previously we reported that LMCT bands of (amine)bis(phenolato)Fe^{III} halide complexes exhibited a noticeable solvent-dependant shift to higher frequencies according to the following trend: methanol < THF < toluene < acetonitrile, where the absorption spectrum in acetonitrile shows this band at the lowest wavelength (496 nm) down from 607 nm in methanol.[78] The influence of solvent polarity on the charge-transfer transitions of (amine)bis(phenolato)-Fe^{III}(acac) complexes was studied. Complexes **1** and **3** were investigated in four different solvents: methanol, THF, toluene, and acetonitrile (Figure 7). The two lower energy bands of complex **1** in four different solvents were found not to vary significantly and were observed around 340 and 550 nm. Specifically, the lowest energy LMCT bands were observed in different solvents at the following wavelengths: toluene (550 nm), THF (547 nm), MeOH (545 nm), and

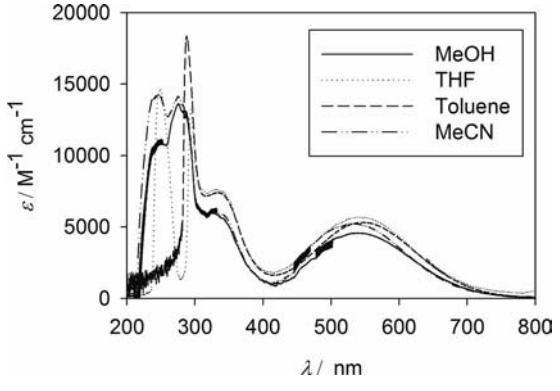


Figure 7. Electronic absorption spectra of **1** in methanol, THF, toluene, and acetonitrile solutions.

MeCN (535 nm). It appears that only a minor solvent-dependant shift was observed because of the multidentate nature of the acac and [O_2N_2] ligands, which prohibits ligand dissociation or structural distortion in solution. This is also a result of the rigidity of the ligand backbone of complex **1**. For complex **3**, the lowest energy bands were found to have a small but more noticeable solvent-dependant shift: toluene (565 nm), MeCN (545 nm), MeOH (543 nm), and THF (534 nm) (Figure 8). The slightly stronger shift may be attributed to the presence of a potentially more labile pendant neutral donor, which may undergo dissociation in good donor solvents such as THF. The stronger solvent dependence observed in the halide containing compounds is possibly a result of the highly labile halide ligands, which have been shown to dissociate in solution.[78] Hence donor solvents are very likely to coordinate to the metal and influence the ligand field.

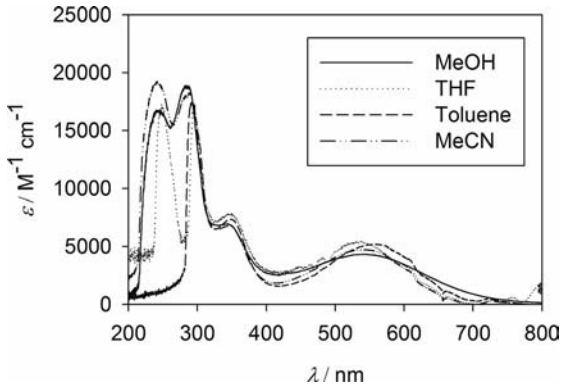


Figure 8. Electronic absorption spectra of **3** in methanol, THF, toluene, and acetonitrile solutions.

Magnetic Properties

The magnetic susceptibility data for crystalline samples of complexes **1**–**5** were collected at room temperature using a Johnson–Matthey magnetic-susceptibility balance. Average magnetic moments in the solid state were adjusted for diamagnetic corrections using Pascal's constants. The magnetic moments [$\mu_{eff} = (8\chi_m T)^{1/2}$] of complexes **1**–**5** are given in Table 3. The magnetic moments of these complexes were in the range of 5.4 to 6.1 μ_B. For complex **4**, the magnetic moment was measured to be 5.4 μ_B, which is slightly lower than expected for a high-spin d^5 ion. As mentioned above, this may be due to the presence of unreacted ligand, which was difficult to separate from the iron complexes. The elemental analysis of the sample used for measurement supports the presence of 6% H_2[**L4**] impurity. Complexes **1**, **2**, **3**, and **5** showed magnetic moments between 5.8 and 6.1 μ_B, which are within the expected range for high-spin octahedral Fe^{III} complexes.

Table 3. Effective magnetic moments for complexes **1**–**5** in the solid state.

Complex	μ_{eff} /μ_B	Complex	μ_{eff} /μ_B
1	6.1	**4**	5.4
2	6.0	**5**	6.0
3	5.8		

Cyclic Voltammetry

Electrochemistry experiments were carried out using a three-compartment electrochemical cell, consisting of a platinum counter electrode, saturated calomel reference electrode (SCE), and a glassy-carbon working electrode. Complexes **1**–**6** were investigated by cyclic voltammetry (CV) in CH_2Cl_2 solutions containing 0.1 M [(nBu)$_4$N]PF_6 as the electrolyte. Results are summarized in Table 4 and representative cyclic voltammograms of **1** and **4** are shown in Figure 9 and Figure 10, respectively. Voltammograms of **2**, **3**, **5**, and **6** are given in Figures S1 to S4 in the Supporting Information. All experiments were performed at a scan rate of 100 mV s^{-1}.

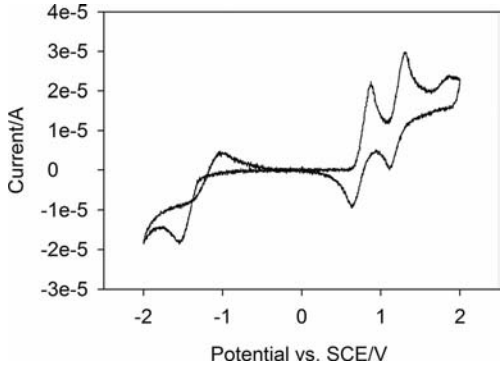


Figure 9. Cyclic voltammogram of **1** in CH_2Cl_2 {0.1 M [(nBu)$_4$N]PF_6} at 25 °C and a scan rate of 100 mV s^{-1}.

The CVs of complexes **1** and **4** are similar and display two reversible oxidation peaks and one quasi-reversible reduction peak, and are consistent with electrochemical studies for a related Fe(acac) complex bearing an (amine)bis(phenolato) ligand with a tetrahydrofurfuryl pendant

Table 4. Electrode peak potentials for oxidation and reduction of complexes **1** to **6**.

Compound	E^2 /V	E^1 /V	E^3 /V
1	$E^2_{1/2}$ = +1.22[a]	$E^1_{1/2}$ = +0.77[a]	$E^3_{p,red}$ = –1.55, $E^3_{p,ox}$ = –1.02
2	$E^2_{p,ox}$ = +1.38, $E^2_{p,red}$ = +1.20	$E^1_{p,ox}$ = +0.78, $E^1_{p,red}$ = +0.31	$E^3_{p,red}$ = –1.55, $E^3_{p,ox}$ = –0.76
3	$E^2_{p,ox}$ = +1.34, $E^2_{p,red}$ = +1.11	$E^1_{p,ox}$ = +0.79, $E^1_{p,red}$ = +0.54	$E^3_{p,red}$ = –1.55, $E^3_{p,ox}$ = –0.79
4	$E^2_{1/2}$ = +1.27[a]	$E^2_{1/2}$ = +0.81[a]	$E^3_{p,red}$ = –1.47, $E^3_{p,ox}$ = –0.72
5	$E^2_{p,ox}$ = +1.51, $E^2_{p,red}$ = +1.51	$E^1_{p,ox}$ = +0.90, $E^1_{p,red}$ = +0.65	$E^3_{p,red}$ = –1.33, $E^3_{p,ox}$ = –0.78
6	$E^2_{p,ox}$ = +1.21, $E^2_{p,red}$ = +1.13	$E^1_{p,ox}$ = +0.83, $E^1_{p,red}$ = +0.67	$E^3_{p,red}$ = –1.10, $E^3_{p,ox}$ = –0.82

[a] Reversible reaction, $E_{1/2}$ is given.

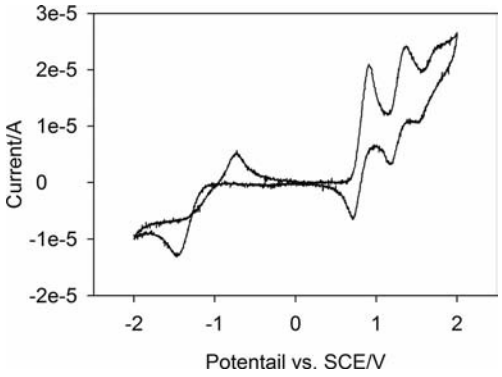


Figure 10. Cyclic voltammogram of **4** in CH_2Cl_2 {0.1 M [$(n$Bu$)_4$N]PF_6} at 25 °C and a scan rate of 100 mV s^{-1}.

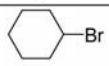
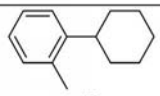
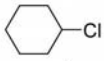
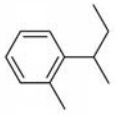
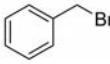
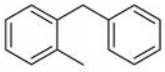
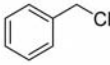
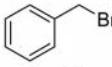
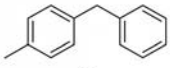
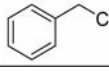
arm.[24] Complexes **2**, **3**, **5**, and **6** exhibit irreversible oxidation responses. These events may be ligand centered redox couples, i.e. phenolate/phenoxyl radical, or a metal centered Fe^{III}/Fe^{IV} redox process, which has been proposed for a related (amine)bis(phenolato)Fe(acac) complex bearing a pyridyl pendant arm.[77] However, metal-centered oxidations are unlikely in these complexes because of difficulties in attaining the less stable Fe^{IV} oxidation state. Complexes **1**–**6** showed quasi-reversible or irreversible redox events at negative potentials. These may be attributed to one-electron metal-centered Fe^{II}/Fe^{III} redox couples.

Cross-Coupling Catalysis Studies

We have reported that Fe^{III} complexes supported by (amine)bis(phenolato) ligands are suitable catalysts for C–C cross-coupling of aryl Grignard reagents with alkyl halides including alkyl chlorides bearing β-hydrogen atoms. Iron(III) halide compounds supported by tetradentate (amine)bis(phenolato) ligands showed good activity as catalysts for the cross-coupling of aryl Grignards with primary and secondary alkyl halides,[68] but the presence of halide groups on the phenolato groups leads to decreased activity.[70] With these systems, diethyl ether was superior to THF as a solvent for the cross-coupling reactions. Also, it was found that reactions performed at room temperature or higher gave superior results to those conducted at lower temperatures.[69] Recent results showed that Fe^{III} compounds supported by tridentate (amine)bis(phenolato) ligands showed better catalytic activity towards selected cross-coupling reactions than their tetradentate counterparts.[69] In some cases, the use of microwave-assisted heating of the reaction mixture improved the yields. Here, we replaced the halide anion in the tetradentate (amine)-bis(phenolato)iron complexes with an acac co-ligand and examined the effect on catalytic activity. The present study employed (amine)bis(phenolato)Fe^{III}(acac) complexes as catalysts for cross-coupling of *o*-tolylmagnesium bromide with secondary alkyl halides in diethyl ether at room temperature or at 100 °C using microwave-assisted heating.

The results of this study are summarized in Table 5. An initial reaction of cyclohexyl bromide with *o*-tolylmagnesium bromide in the presence of complex **1** gave an excellent yield of cross-coupled product after 30 min at room temperature (Entry 1). Cyclohexyl chloride could also be used as an electrophilic partner, but yields of product varied depending on the catalyst used. Catalysts employing a ligand with an amine pendent arm showed a relatively lower yield of cross-coupled products (Entries 2 and 3). However, ligands with ether pendent arms gave better catalysts showing excellent yields (up to 96%) of cross-coupled products (Entries 4–6). There are few reports of Kumada-type cross-coupling using cyclohexyl chloride. Bedford and coworkers showed good to modest yields (70–80%) of cross-coupled products between cyclohexyl chloride and *p*-tolylmagnesium bromide using different Fe-based catalysts such as Fe(salen) complexes, $FeCl_3$/amine, and Fe nanoparticles.[65,88,89] Nakamura and coworkers obtained a 99% yield of cross-coupled products from cyclohexyl chloride and phenylmagnesium bromide while using $FeCl_3$/TMEDA

Table 5. Cross coupling of aryl Grignard reagents with alkyl halides catalyzed by (amine)bis(phenolato)Fe(acac) complexes.[a]

Entry	Catalyst	Alkyl halide	Product	%Yield
1	**1**			97[b]
2	**2**		"	33
3	**3**	"	"	55
4	**4**	"	"	96
5	**5**	"	"	80
6	**6**	"	"	79
7	**1**			17
8	**2**	"	"	12
9	**3**	"	"	16
10	**4**	"	"	13
11	**5**	"	"	16
12	**6**	"	"	14
13	**5**		"	12
14	$Fe(acac)_3$	"	"	17
15	**4**			60[b]
16	**4**		"	52[b]
17	**4**			49[b]
18	**4**		"	37[b]

[a] Reaction conditions: catalyst (0.05 mmol), alkyl halide (1.00 mmol), Et_2O (1.50 mL), Grignard reagent (2.00 mmol), dodecane as internal standard (1.0 mmol), MW heating 100 °C for 10 min. The reaction was quenched by the addition of 2.50 mL of 1.00 M HCl(aq.). The product yields were quantified by GC–MS and confirmed by NMR spectroscopy. [b] Stirred at 25 °C for 30 min.

(TMEDA = tetramethylethylenediamine) as the catalyst.[58] Their procedure required the slow addition of a Grignard reagent to the reaction mixture. Also, they noticed that TMEDA suppressed the formation of undesirable side products via the loss of hydrogen halide from the alkyl halides.

We then investigated complexes **1**–**6** for cross-coupling of the acyclic secondary alkyl halide 2-bromobutane with *o*-tolylmagnesium bromide. In these reactions, poor yields (12–17%) of cross-coupled products were observed (Entries 7 to 12). This was in stark contrast to the promising results observed by Nakamura and coworkers for the cross-coupling of 2-bromobutane with phenylmagnesium bromide, where a 94% yield of cross-coupled product was obtained using $FeCl_3$/TMEDA.[58] Recently, Cahiez and coworkers reported using the combination of $Fe(acac)_3$ and TMEDA/HMTA (HMTA = hexamethylenetetramine) (10% TMEDA:5% HMTA vs. alkyl halide).[51] In both cases, Grignard reagents were added slowly to the reaction mixture. Whereas 2-bromobutane and 2-iodobutane gave excellent yields, only a trace amount of cross-coupled product was obtained using 2-chlorobutane as the alkyl halide. Using our system, 12% of cross-coupled product was obtained with 2-chlorobutane and *o*-tolylmagnesium bromide (Entry 13), but our catalysts did not give good results for 2-bromobutane either. $Fe(acac)_3$ was shown to give excellent catalytic activity for the cross-coupling of secondary alkyl halides and aryl Grignard reagents in the presence of the additives TMEDA and HMTA.[51] Also, $Fe(acac)_3$ without any additives is an efficient catalyst for the cross-coupling of aryl Grignard reagents and alkyl halides possessing β-hydrogens.[60] However, $Fe(acac)_3$, under our conditions, gave only a 17% yield of cross-coupled product using 2-bromobutane (Entry 14).

Recently Bedford and coworkers reported iron catalyzed Negishi coupling of benzyl halides with diarylzinc and Fe–Zn cocatalyzed Suzuki coupling of benzyl halides with tetraarylborate.[90,91] We examined the cross-coupling of benzyl halides (Br and Cl) with *o*-tolylmagnesium bromide and *p*-tolylmagnesium bromide in the presence of complex **4**. Reaction of benzyl bromide with *o*-tolyl Grignard gave a 60% yield of cross-coupled product after 30 min at room temperature (Entry 15). Benzyl chloride gave a similarly moderate yield (Entry 16). Using *p*-tolylmagnesium bromide, however, gave slightly lower yields than *o*-tolylmagnesium bromide with the respective benzyl halide (Entries 17 and 18). These preliminary studies show (amine)bis(phenolato)Fe^{III}(acac) complexes give some catalytic activity towards cross coupling of aryl Grignard reagents with alkyl halides. However, for the substrates studied thus far, they are generally inferior to simple $Fe(acac)_3$-containing systems[39,50,51,55,60,66,67] or (amine)bis(phenolato)iron halide complexes previously reported by us.[68,92]

Conclusions

A series of Fe^{III}(acac) complexes supported by (amine)bis(phenolato) ligands has been synthesized and characterized. Representative complexes **1**, **2**, **3**, and **5** have been structurally characterized by single-crystal X-ray diffraction and all complexes reported are six coordinate and exhibit distorted octahedral geometries. Moreover, all of these paramagnetic complexes have been analytically verified by elemental analysis and MALDI-TOF mass spectrometry. Magnetic moment measurements indicate high-spin d^5 iron centers. Electronic absorption spectra in the UV/Vis range exhibit strong charge-transfer bands, which are slightly solvent dependant. Cyclic voltammograms of these complexes show reversible ligand-centered redox processes. Preliminary studies of all the complexes for the catalytic cross-coupling of aryl Grignard reagents with alkyl halides were performed and showed that the coupling of *o*-tolylmagnesium bromide with cyclohexyl chloride was influenced by the (amine)bis(phenolato) ligand employed. Generally, the yield of arylcyclohexane was high. However, acyclic 2-halobutane showed poor yields of product whereas benzyl halides showed moderate activity for cross-coupling. Investigations for other substrates are currently in progress.

Experimental Section

General Considerations: Unless otherwise stated, all manipulations were performed in air. Reagents were purchased either from Aldrich or Alfa Aesar and used without further purification. The syntheses of H_2**[L1]**–H_2**[L6]** were conducted by a modified literature procedure in water,[75,76] and a representative synthesis of H_2**[L5]** is given below. $Fe(acac)_3$ (99%) was purchased from Strem Chemicals. Anhydrous diethyl ether was purified using an MBraun solvent purification system.

Instrumentation: NMR spectra were recorded in $CDCl_3$ with a Bruker Avance III 300 MHz instrument with a 5 mm-multinuclear broadband observe (BBFO) probe. MALDI-TOF MS spectra were performed using an ABI QSTAR XL Applied Biosystems/MDS hybrid quadrupole TOF MS/MS system equipped with an oM-ALDI-2 ion source. Samples were prepared at a concentration of 10.0 mg mL^{-1} in toluene. Anthracene was used as the matrix, which was mixed at a concentration of 10.0 mg mL^{-1}. UV/Vis spectra were recorded with an Ocean Optics USB4000+ fiber optic spectrophotometer. IR spectra were recorded with a Bruker Alpha IR spectrometer equipped with a diamond crystal ATR module. Room temperature magnetic moments were determined using a Johnson-Matthey magnetic susceptibility balance. The data were corrected for the diamagnetism of all atoms and the balance was calibrated using $Hg[Co(NCS)_4]$. Cyclic voltammetry measurements were performed with a Model HA 301 Hokuto Deuko potentiostat/galvanostat. Elemental analyses were carried out by Canadian Microanalytical Services Ltd. Delta, BC, Canada. Crystal structures were obtained with an AFC8-Saturn 70 single-crystal X-ray diffractometer from Rigaku/MSC, equipped with an X-stream 2000 low-temperature system, a SHINE optic, and Mo-K_α radiation. Gas chromatography mass spectrometry (GC–MS) analyses were performed using an Agilent Technologies 7890GC system coupled to an Agilent Technologies 5975C mass selective detector (MSD). The chromatograph is equipped with an electronic pressure control, split/splitless and on-column injectors, and an HP5 MS column. Microwave-heated reactions were performed using a Biotage Initiator™ eight microwave synthesizer.

H_2[L5]: The proligand H_2**[L5]** was synthesized following the literature procedure[76] but no spectroscopic characterization was re-

ported in the original paper, therefore a representative synthesis and NMR characterization of the proligands are given here. 2-Methoxyethylamine (4.63 g, 0.0616 mol) was added to a vigorously stirred mixture of 2-*tert*-butyl-4-methylphenol (20.236 g, 0.1232 mol) and 37% aqueous formaldehyde (9.17 mL, 0.123 mol) in water (50 mL). The mixture was heated to reflux for 12 h. Upon cooling, a large quantity of beige solid formed. The solvents were decanted and the remaining solid residue was washed with cold methanol to give a white powder (25.00 g, 95% yield). Crystalline product was obtained by slow cooling of a hot diethyl ether solution. ^{1}H NMR (300 MHz, 295 K): δ = 8.40 (s, 2 H, OH), 7.0 (d, $^4J_{HH}$ = 1.5 Hz, 2 H, ArH), 6.72 (d, $^4J_{HH}$ = 1.5 Hz, 2 H, ArH), 3.71 (s, 4 H, $ArCH_2$), 3.52 (t, $^3J_{HH}$ = 5.09 Hz, 2 H, CH_2O), 3.46 (s, 3 H, OCH_3), 2.73 (t, $^3J_{HH}$ = 5.09 Hz, 2 H, NCH_2), 2.24 (s, 6 H, $ArCH_3$), 1.41 [s, 18 H, $ArC(CH_3)_3$] ppm. ^{13}C{H} NMR (75 MHz, 295 K): δ = 153.04 (Ar-*C*-OH), 136.83 (Ar-*C*H), 128.79 (Ar-*C*H), 127.36 (Ar-*C*H), 127.24 (Ar-*C*H), 122.44 (Ar-*C*-CH_2-N), 71.51 (Ar-*C*H_2), 58.86 (O*C*H_3), 51.37 (N-CH_2–*C*H_2–O), 57.62 (N-*C*H_2–CH_2–O), 34.71 [*C*$(CH_3)_3$], 29.57 [C(*C*$H_3)_3$], 20.78 (Ar-*C*H_3) ppm.

Synthesis of Metal Complexes

[L1]Fe(acac) (1): A solution of Fe(acac)$_3$ (1.03 g, 2.92 mmol) in methanol was added to a methanol slurry of recrystallized $H_2[N_2O_2]^{BuBu}$, H_2[**L1**], (1.53 g, 2.92 mmol) while stirring. This resulted in a brown-red solution. Triethylamine (590 mg, 5.84 mmol) was added to this solution followed by heating to 64 °C for 0.5 h. The color of the solution changed to dark purple. The solvent was evaporated and the residue dissolved in acetone (50 mL). Addition of an equal volume of H_2O precipitated the complex, which was collected on a frit and dried in vacuo to obtain 1.20 g (61%) of a dark-purple powder. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of **1** in a 1:1 mixture of methanol and diethyl ether. $C_{39}H_{61}FeN_2O_4$ (677.77): calcd. C 69.11, H 9.07, N 4.13; found C 68.51, H 9.11, N 4.29. MALDI-TOF MS (poitive mode, anthracene): *m*/*z* (% of ion) = 677.40 (25) $[M]^+$, 577.35 (100) [M – acac – 1]$^+$. UV/Vis (CH_3OH): λ_{max} (ε, $dm^3 mol^{-1} cm^{-1}$) = 237 (16600), 279 (17325), 327 (7009), 540 (4614) nm. IR (neat): $\tilde{\nu}$ = 2954, 2902, 2865, 1584, 1521, 1465, 1441, 1375, 1360, 1307, 1274, 1250, 1237, 1203, 1167, 1129, 1017, 967, 929, 914, 875, 840, 808, 791, 780, 766, 748, 612, 545, 469, 450, 431 cm^{-1}. μ_{eff} (solid, 21.8 °C): 6.1 μ_B.

[L2]Fe(acac) (2): A solution of Fe(acac)$_3$ (2.36 g, 6.68 mmol) in methanol was added to a methanol slurry of recrystallized $H_2[O_2NN']^{BuBuNMe2}$, H_2[**L2**], (3.51 g, 6.68 mmol) while stirring. This resulted in a brown-red solution. Triethylamine (1.35 g, 13.37 mmol) was added to this solution followed by heating to 64 °C for 0.5 h. The color of the solution changed to dark purple. The solvent was evaporated and the residue dissolved in acetone (50 mL). Addition of an equal volume of H_2O precipitated the complex, which was collected on a frit and dried in vacuo to obtain 3.02 g (67%) of a dark-purple powder. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of **2** in a 1:1 mixture of methanol and diethyl ether. $C_{39}H_{61}FeN_2O_4$ (677.77): calcd. C 69.11, H 9.07, N 4.13; found C 69.44, H 9.13, N 4.18. MALDI-TOF MS (positive mode, anthracene); *m*/*z* (% of ion) = 677.40 (9) $[M]^+$, 577.35 (9) [M – acac – 1]$^+$, 466.35 (100) [M – acac – Fe – C_3H_9N + 2H]$^+$. UV/Vis (CH_3OH): λ_{max} (ε, $dm^3 mol^{-1} cm^{-1}$) = 236 (16626), 279 (15865), 316 (4306), 535 (2441) nm. IR (neat): $\tilde{\nu}$ = 2951, 2903, 2866, 1587, 1520, 1479, 1465, 1442, 1415, 1376, 1360, 1303, 1284, 1268, 1256, 1228, 1201, 1165, 1125, 1107, 1023, 925, 876, 840, 824, 809, 775, 748, 666, 544, 472, 429, 406 cm^{-1}. μ_{eff} (solid, 21.8 °C): 6.0 μ_B.

[L3]Fe(acac) (3): A solution of Fe(acac)$_3$ (2.41 g, 6.81 mmol) in methanol was added to a methanol slurry of recrystallized $H_2[O_2NN']^{BuMeNMe2}$, H_2[**L3**], (3.01 g, 6.81 mmol) while stirring. This resulted in a brown-red solution. Triethylamine (1.37 g, 13.6 mmol) was added to this solution followed by heating to 64 °C for 0.5 h. The color of the solution changed to dark purple. The solvent was evaporated and the residue was dissolved in acetone (50 mL). Addition of an equal volume of H_2O precipitated the complex, which was collected on a frit and dried in vacuo to obtain 2.85 g (71%) of a dark-purple powder. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of **3** in a 1:1 mixture of methanol and diethyl ether. $C_{33}H_{49}FeN_2O_4$ (593.61): calcd. C 66.77, H 8.32, N 4.72; found C 66.91, H 8.24, N 4.76. MALDI-TOF MS (positive mode, anthracene); *m*/*z* (% of ion) = 593.30 (8) $[M]^+$, 496.26 (16) [M – acac]$^+$. UV/Vis (CH_3OH): λ_{max} (ε, $dm^3 mol^{-1} cm^{-1}$) = 243 (16747), 284 (18893), 343 (6952), 522 (4326) nm. IR (neat): $\tilde{\nu}$ = 2949, 2905, 1585, 1519, 1462, 1434, 1374, 1301, 1274, 1207, 1151, 1019, 927, 862, 825, 770, 665, 597, 545, 431, 403 cm^{-1}. μ_{eff} (solid, 21.8 °C): 5.8 μ_B.

[L4]Fe(acac) (4): A solution of Fe(acac)$_3$ (2.28 g, 6.46 mmol) in methanol was added to a methanol slurry of recrystallized $H_2[O_2NO]^{BuBuMeth}$, H_2[**L4**], (3.30 g, 6.46 mmol) while stirring. This resulted in a brown-red solution. Triethylamine (1.31 g, 12.9 mmol) was added to this solution followed by heating to 64 °C for 0.5 h. The color of the solution changed to dark purple. The solvent was evaporated and the residue was dissolved in acetone (50 mL). Addition of an equal volume of H_2O precipitated the complex, which was collected on a frit and dried in vacuo to obtain 2.52 g (59%) of a dark-purple powder. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of **4** in a 1:1 mixture of methanol and diethyl ether. $C_{38}H_{58}FeNO_5$ (664.73): calcd. C 68.66, H 8.79, N 2.11. Calcd for **4**·0.06(H_2[**L6**]): C 69.05, H 8.87, N 2.13; found C 69.09, H 8.85, N 2.19. MALDI-TOF MS (positive mode, anthracene); *m*/*z* (% of ion) = 664.37 (36) $[M]^+$, 564.32 (7) [M – acac – 1]$^+$, 511.41 (57) $[L_3]^+$, 466.37 (100) [M – acac – Fe – C_2H_5O + 2H]$^+$. UV/Vis (CH_3OH): λ_{max} (ε, $dm^3 mol^{-1} cm^{-1}$) = 235 (14575), 277 (16612), 340 (5142), 522 (2887) nm. IR (neat): $\tilde{\nu}$ = 2954, 2904, 2868, 1585, 1521, 1474, 1442, 1381, 1363, 1299, 1273, 1233, 1202, 1165, 1123, 1096, 1018, 932, 878, 840, 771, 657, 549, 481, 437, 407 cm^{-1}. μ_{eff} (solid, 18.2 °C): 5.4 μ_B.

[L5]Fe(acac) (5): A solution of Fe(acac)$_3$ (2.57 g, 7.27 mmol) in methanol was added to a methanol slurry of recrystallized $H_2[O_2NO]^{BuMeMeth}$, H_2[**L5**], (3.11 g, 7.27 mmol) while stirring. This resulted in a brown-red solution. Triethylamine (1.56 g, 14.5 mmol) was added to this solution followed by heating to 64 °C for 0.5 h. The color of the solution changed to dark purple. The solvent was evaporated and the residue was dissolved in acetone (50 mL). Addition of an equal volume of H_2O precipitated the complex, which was collected on a frit and dried in vacuo to obtain 2.98 g (71%) of a dark-purple powder. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of **5** in a 1:1 mixture of methanol and diethyl ether. $C_{32}H_{46}FeNO_5$ (580.57): calcd. C 66.20, H 7.99, N 2.41; found C 66.10, H 8.08, N 2.42. MALDI-TOF MS (positive mode, anthracene); *m*/*z* (% of ion) = 580.27 (29) $[M]^+$, 480.22 (26) [M – acac – 1]$^+$, 382.28 (100) [M – acac – Fe – C_2H_5O + 2H]$^+$. UV/Vis (CH_3OH): λ_{max} (ε, $dm^3 mol^{-1} cm^{-1}$) = 232 (10275), 282 (10771), 342 (3263), 522 (1742) nm. IR (neat): $\tilde{\nu}$ = 2953, 2910, 1581, 1521, 1469, 1437, 1365, 1298, 1270, 1232, 1204, 1150, 1094, 1059, 1016, 927, 861, 826, 770, 663, 595, 549, 434, 406 cm^{-1}. μ_{eff} (solid, 18.8 °C): 6.0 μ_B.

[L6]Fe(acac) (6): A solution of Fe(acac)$_3$ (2.68 g, 7.60 mmol) in methanol was added to a methanol slurry of recrystallized $H_2[O_2NO]^{MeMeMeth}$, H_2[**L6**], (2.61 g, 7.60 mmol) while stirring. This resulted in a brown-red solution. Triethylamine (1.54 g,

15.2 mmol) was added to this solution followed by heating to 64 °C for 0.5 h. The color of the solution changed to dark purple. The solvent was evaporated and the residue was dissolved in acetone (50 mL). Addition of an equal volume of H_2O precipitated the complex, which was collected on a frit and dried in vacuo to obtain 2.89 g (77%) of a dark-purple powder. The product contained a consistently high degree of contamination with proligand H_2[**L6**]. Therefore, satisfactory combustion analyses could not be obtained and crystals of proligand always contaminated crystals of the complex. MALDI-TOF MS (positive mode, anthracene); *m*/*z* (% of ion) = 496.18 (20) $[M]^+$, 397.13 (50) $[M - acac]^+$. UV/Vis (CH_3OH): λ_{max} (ε, $dm^3 mol^{-1} cm^{-1}$) = 240 (14684), 277 (19617), 344 (4705), 544 (3088) nm. IR (neat): $\tilde{\nu}$ = 2912, 2845, 1570, 1520, 1478, 1438, 1364, 1306, 1267, 1226, 1158, 1117, 1073, 1016, 929, 866, 809, 768, 663, 600, 549, 507, 434, 411 cm^{-1}.

General Methods for Cross-Coupling Catalysis:

Method A. Procedure for cross-coupling at room temperature under an inert atmosphere: The selected iron complex (0.10 mmol) in CH_2Cl_2 (3 mL) was added to a 45 mL Schlenk tube and the solvent removed in vacuo. Et_2O (5 mL) and alkyl halide (2.0 mmol) were added to the catalyst under dry nitrogen. A solution of aryl Grignard reagent (4.0 mmol) was added dropwise under vigorous stirring. The resulting mixture was stirred for 30 min, then dodecane (2.0 mmol as internal standard) was added and the reaction was quenched with HCl(aq.) (1.0 M, 5 mL). The organic phase was extracted with Et_2O (5 mL) and dried with $MgSO_4$. The mixture was analyzed by GC–MS and NMR spectroscopy.

Method B. Procedure for cross-coupling under microwave-heating: The selected iron complex (0.05 mmol) and a magnetic stir bar were added to a Biotage™ microwave vial, which was sealed with a septum cap under an inert atmosphere. A solution of alkyl halide (1.0 mmol) in Et_2O (2.5 mL) was injected into the vial, followed by a Grignard reagent solution (2.00 mmol). The mixture was heated in a Biotage Initiator™ Eight Microwave Synthesizer using the following parameters: time = 10 min; T = 100 °C; pre-stirring = off; absorption level = normal; fixed hold time = on. Upon completion, dodecane (1.00 mmol, internal standard) was added to the mixture followed by the addition of HCl(aq.) (1.0 M, 2.5 mL) for quenching. The product yields were quantified by GC–MS and NMR spectroscopy.

X-ray Crystallography

Crystallographic data for compounds **1**, **2**, **3**, **5**, and H_2[**L6**] are summarized in Table 6. All data collections were performed with a Rigaku AFC8-Saturn 70 diffractometer equipped with a CCD area detector, using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Suitable crystals were selected and mounted on glass fibers using Paratone-N oil and freezing to –120 °C, or –100 °C in the case of H_2[**L6**]. The data were processed[93,94] and corrected for Lorentz and polarization effects and absorption.[95] Neutral atom scattering factors for all non-hydrogen atoms were taken from the international tables for the X-ray crystallography analysis.[96] All structures were solved by direct methods using SIR92[97] and expanded using Fourier techniques (DIRDIF99).[98] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model.

Anomalous dispersion effects were included in F_{calc};[99] the values used for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[100] The values used for the mass attenuation coefficients are those of Creagh and Hubbell.[101] All calculations were performed using the CrystalStructure[102,103] crystallographic software package except for refinement, which was performed using the SHELXL-97 program.[104] In complexes **2** and **3**, two chemical formula unit moieties are present in the asymmetric unit, and therefore Z was set to 8 in order to reflect the formula per one moiety. In complex **2**, one *tert*-butyl group is disordered over two sites. This was refined in two parts; PART 1 (C64, C65, C66, and corresponding H-atoms) are present at 0.8-occupancy, while PART 2 (C67, C68, C69, and corresponding H-atoms) are present at 0.2-occupancy. ISOR restraints were introduced in order to prevent C(67) and C(69) from becoming non-definite positive. Structural illustrations were created using ORTEP-III for Windows.[105]

Table 6. Crystallographic and structural refinement data for compounds **1**, **2**, **3**, **5**, and H_2[**L6**].

	1	**2**	**3**	**5**	H_2[**L6**]
Empirical formula	$C_{39}H_{61}FeN_2O_4$	$C_{39}H_{61}FeN_2O_4$	$C_{33}H_{49}FeN_2O_4$	$C_{32}H_{46}FeNO_5$	$C_{21}H_{29}NO_3$
M_r /g mol^{-1}	677.77	677.77	593.61	580.57	343.45
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	orthorhombic
a /Å	13.9905(15)	13.7115(19)	10.158(3)	9.5103(12)	8.7923(5)
b /Å	20.485(3)	23.240(3)	23.434(7)	23.403(3)	13.8917(9)
c /Å	27.491(3)	27.809(4)	27.388(8)	14.5291(19)	16.3005(10)
α /°	90	90	90	90	90
β /°	90	115.343(3)	90.045(8)	104.444(2)	90
γ /°	90	90	90	90	90
Unit cell volume /Å^3	7878.9(16)	8008.7(19)	6520(3)	3131.5(7)	1990.9(2)
Temperature /K	153(2)	153(2)	153(2)	153(2)	173(2)
Space group	*Pbca*	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
Z	8	8	8	4	4
Radiation type	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α	Mo-K_α
Absorption coefficient, μ /mm^{-1}	0.421	0.414	0.499	0.519	0.076
No. of reflections measured	80834	106542	49036	41710	21544
No. of independent reflections	8155	14074	11284	7144	5472
R_{int}	0.0929	0.1091	0.0796	0.0318	0.0263
Final R_1 values $[I > 2\sigma(I)]$[a]	0.0923	0.1093	0.1100	0.0396	0.0473
Final $wR(F^2)$ values $[I > 2\sigma(I)]$[a]	0.1549	0.1999	0.2564	0.1049	0.1417
Final R_1 values (all data)	0.0961	0.1193	0.1183	0.0413	0.0487
Final $wR(F^2)$ values (all data)	0.1563	0.2045	0.2619	0.1068	0.1444
Goodness of fit on F^2	1.455	1.342	1.176	1.086	1.076

[a] $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$; $wR(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$.

CCDC-827726 (for **1**), -827727 (for **2**), -827728 (for **3**), -827729 (for **5**), and -827730 (for H_2[**L6**]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Cyclic voltammograms of complexes **2**, **3**, **5**, and **6**.

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