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Synthesis and Characterization of a Sterically Encumbered Homoleptic Tetraalkyliron(III) Ferrate Complex

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Abstract

Homoleptic iron-alkyl complexes have been implicated as key intermediates in iron-catalyzed cross-coupling with simple iron salts. Tetraalkyliron(III) ferrate species have been shown to be accessible with either methyl or benzyl ligands, where the former complex is $S = 3/2$ and distorted square planar while the latter is a $S = 5/2$ distorted tetrahedral species. In the current study, a new tetraalkyliron(III) complex is synthesized containing modified methylene substituents that incorporate large trimethylsilyl (TMS) groups to further probe steric and electronic ligand effects in tetraalkyliron(III) complexes by increasing the electron-donating ability of the ligand while retaining steric bulk. Detailed structural and DFT studies provide insight into electronic structure and bonding of the four-coordinate trimethylsilylmethyl iron(III) complex compared to the previously reported analogs containing methyl and benzyl ligands.

Graphical Abstract

The tetraalkyliron(III) complex, $[\text{Li}(\text{THF})_2][\text{Fe}(\text{CH}_2\text{Si}(\text{CH}_3)_3)_4]$, has been synthesized containing modified methylene substituents that incorporate large trimethylsilyl (TMS) groups to further probe steric and electronic ligand effects in tetraalkyliron(III) complexes by increasing the electron-donating ability of the ligand while retaining steric bulk. Detailed structural and DFT

Appendix A. Supplementary data

CCDC 1862588 contains the supplementary crystallographic data for compound 1. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223–336–033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version.

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studies provide insight into electronic structure and bonding of this complex compared to the previously reported analogs containing methyl and benzyl ligands.

Keywords

iron-alkyl complexes; X-ray crystallography; DFT calculations; Mössbauer spectroscopy

1. Introduction

Iron-catalyzed cross-coupling has continued to be an active sub-field of iron catalysis research due to the potential to achieve low-cost, sustainable cross-coupling transformations for organic synthesis.^{2–7} In addition to advances in methodology development, significant research has recently focused on mechanistic studies, including insight into active catalyst structure, as well as ligand and additive effects.^{8–14} Such insights are critical in order to provide a fundamental basis to facilitate improvements in current iron cross-coupling systems, as well as to inspire the development of new catalysts and methodologies to greatly expand the scope and utility of iron in C-C cross-coupling.

Homoleptic η^1 -bound organoiron species have been implicated as key intermediate complexes in iron-catalyzed cross-coupling, both as active participants in reactions with electrophile to generate cross-coupled products, as well as progenitors of more reactive iron complexes.^{1,13,15–20} With an increase in the number of these species being reported, detailed characterization including electronic structure calculations of iron-alkyl bonding across a broad array of spin and oxidation states is desirable in order to understand contributions of electronic structure and bonding to reactivity in cross-coupling involving simple iron salts and alkyl nucleophiles. Towards this goal, recent reports of homoleptic mono- and multimeric iron-alkyl species have broadened the scope and understanding of possible iron-alkyl species.^{1,13,16,18,20} In particular, these studies have focused on iron species formed from reactions of iron salts and simple alkyl substituents (e.g. methyl), though an additional example of a higher molecular weight substituent (e.g. benzyl) has also been reported (Figure 1). For reactions of FeCl_3 and methylmagnesium bromide (MeMgBr), it has been shown that a distorted square planar tetramethyliron(III) ferrate, $[\text{FeMe}_4]^-$, can be generated in low temperature reactions (i.e. -78°C). While not reactive towards electrophile at temperatures where it is stable, warming towards room temperature results in transformation of this species to $[\text{Fe}_8\text{Me}_{12}]^-$ with the concomitant formation of ethane.¹ Interestingly, density functional theory (DFT) studies of the $S = 3/2$ $[\text{FeMe}_4]^-$ complex compared to the bulkier $S = 5/2$ distorted tetrahedral tetrabenzyliron(III) ferrate species ($[\text{FeBn}_4]^-$) previously reported by Bedford¹⁹ determined that while a distorted square planar geometry is necessary in order to maximize the charge donation of the four alkyl substituents to the iron center (including for the tetrabenzyl case), $[\text{FeBn}_4]^-$ adopts the distorted tetrahedral geometry as steric clashing of the benzyl ligands decreases the overall energy of the sextet complex (distorted tetrahedral) compared to that of the quartet complex (distorted square planar).

In the current study, we have sought to expand upon our understanding of the effect of the nature of alkyl substituents on electronic structure and bonding in homoleptic iron(III) alkyl

complexes, including the previously identified steric effect for benzyl ligands, by modifying the methylene substituents to incorporate large trimethylsilyl (TMS) groups to provide a stronger electron donor ligand while maintaining increased steric bulk relative to simple methyl ligands. Hence, the geometry and electronic structure of the resulting homoleptic $[\text{Fe}(\text{CH}_2\text{TMS})_4]^-$ complex would enable further evaluation of the relative contributions of alkyl ligand donation ability versus ligand steric effects in determining structure and bonding in tetraalkyliron(III) complexes. Using in situ spectroscopy (^{57}Fe Mössbauer and EPR) to determine appropriate crystallization conditions for the formation of the desired homoleptic tetraalkyl complex, we report the synthesis and characterization of a new homoleptic alkyliron(III) ferrate complex via the reaction of $\text{Fe}(\text{acac})_3$ and trimethylsilylmethyl lithium. Structural analysis and DFT calculations provide insight into the electronic structure and bonding of the trimethylsilylmethyl iron(III) complex compared to the previously reported analogs containing methyl and benzyl ligands.

2. Experimental

2.1 General Considerations.

All reagents were purchased from commercial sources. All air and moisture sensitive manipulations were carried out in an MBraun inert-atmosphere (N_2) dry box equipped with a direct liquid nitrogen inlet line. All anhydrous solvents were further dried using activated alumina/4Å molecular sieves and stored under an inert atmosphere over molecular sieves. $^{57}\text{Fe}(\text{acac})_3$ was synthesized following a literature procedure using ^{57}Fe metal (95% enriched) purchased from Isoflex. Low-temperature reactions (-78°C) were performed in a cold well inside of the glovebox using a liquid N_2 /ethyl acetate mixture. ^1H NMR spectrum was recorded on a Bruker Avance 400 MHz (400 MHz, ^1H).

2.2 Preparation of $[\text{Li}(\text{THF})_2][\text{Fe}(\text{CH}_2\text{Si}(\text{CH}_3)_3)_4]$ (**1**).

In a scintillation vial fitted with a stir bar $\text{Fe}(\text{acac})_3$ (70 mg, 0.14 mmol) was dissolved in minimal THF (0.4 mL). The red solution was cooled to -78°C . Once the temperature equilibrated, the reaction mixture was transferred to a stir plate at RT and treated with 5 equiv of $\text{LiCH}_2\text{Si}(\text{CH}_3)_3$ (1.0 M in pentane). The yellow solution was left to continue stirring at RT for 5 minutes followed by cooling to -78°C . After 1 hour at -78°C , 4.0 mL cold pentane was added. The yellow solution was filtered through Celite (pre-cooled to -78°C) and the yellow filtrate stored at -80°C for one week rendering orange crystalline blocks. The long-term solid-state stability of this complex is currently unknown.

****Handling of temperature sensitive crystals of **1** for X-ray diffraction.—**

Manipulations were carried out inside a nitrogen purged glovebag. Scintillation vials with crystalline material of **1** were stored in an aluminum Pie-Block containing dry ice. A specialized aluminum block with a hollow internal chamber, equipped with inlet and outlet nozzles, was cooled by the passage of liquid nitrogen through the block. Microscope slides coated with SilOil were precooled on the cold aluminum block, upon which an aliquot of cold solution from the scintillation vial was pipetted. Crystalline specimens for X-ray diffraction were examined microscopically. Appropriate single crystals were removed from

the glass slide with a goniometer pin and transported to the diffractometer while being held over a hand Dewar containing liquid nitrogen.

2.3 Electron Paramagnetic Resonance (EPR) Spectroscopy.

All samples for EPR spectroscopy were prepared in an inert atmosphere glove box equipped with a liquid nitrogen fill port to enable sample freezing to 77 K within the glovebox. EPR samples were prepared in 4 mM OD suprasil quartz EPR tubes from Wilmad Labglass. Samples for spin integration utilized high precision suprasil quartz tubes to allow for direct comparison of intensities between different samples. All samples for EPR spectroscopy were 3 mM iron. X-band EPR spectra were recorded on a Bruker EMXplus spectrometer equipped with a 4119HS cavity and an Oxford ESR-900 helium flow cryostat. The instrumental parameters employed for all samples were as follows: 1 mW power; time constant 41 ms; modulation amplitude 8 G; 9.38 GHz; modulation frequency 100 kHz.

2.4 Mössbauer Spectroscopy.

Frozen solution samples for ^{57}Fe Mössbauer spectroscopy were prepared from 3 mM $^{57}\text{Fe}(\text{acac})_3$ in THF. All samples were prepared in an inert atmosphere glovebox equipped with a liquid nitrogen fill port to enable sample freezing to 77 K within the glovebox. Each sample was loaded into a Delrin Mössbauer sample cup for measurements and loaded under liquid nitrogen. Low temperature ^{57}Fe Mössbauer measurements were performed using a See Co. MS4 Mössbauer spectrometer integrated with a Janis SVT-400T He/N₂ cryostat for measurements at 80 K. Isomer shifts were determined relative to α -Fe at 298 K. All Mössbauer spectra were fit using the program WMoss (SeeCo). Errors of the fit analyses were the following: $\delta \pm 0.02$ mm/s and $E_Q \pm 3\%$.

2.5 Electronic Structure Calculations.

Spin unrestricted density functional theory (DFT) calculations were performed with the Gaussian 09 package.²¹ All geometry optimization calculations were performed with the B3LYP^{22,23} functional and def2-TZVP^{24–27} basis set on all atoms. Calculations included the Li(THF)₂ subunit to determine coordination effects. The geometries of **1** for spin state $S = 5/2$ was optimized starting from X-ray crystal structure coordinates. All optimized geometries had frequencies found to be real.

Further calculations of MOs and energies used the B3LYP^{27,28} with the def2-TZVP basis set on all atoms. Energies given include zero-point and thermal corrections. Orbitals from the Gaussian calculations were plotted with the ChemCraft program. Atomic charges and spin densities were calculated using Mulliken population analysis methods (MPA). The analysis of the MO compositions through the utilizations of fragment molecular orbitals and the charge decomposition analysis were performed using AOMix-CDA.^{29,30}

3. Results and Discussion

Since previous reports from our group demonstrated $[\text{FeMe}_4]^-$ could be synthesized via reaction of simple ferric salts with MeMgBr,¹ initial synthetic efforts towards the preparation of $[\text{Fe}(\text{CH}_2\text{TMS})_4]^-$ included reactions of $\text{Fe}(\text{acac})_3$ and

trimethylsilylmethylmagnesium chloride in THF, while alternative nucleophiles such as such as trimethylsilylmethyl lithium (TMSCH₂Li) were also evaluated using ⁵⁷Fe Mössbauer spectroscopy of freeze-trapped reaction solutions. To a solution of ⁵⁷Fe(acac)₃ in THF (cooled to -78 °C) either 5 equiv of TMSCH₂Li (1.0 M in pentane) or TMSCH₂MgCl (1.0 M in Et₂O) was added in one portion. The reaction mixture was subsequently stirred for 5 minutes at RT followed by rapid freeze-trapping of a reaction aliquot for ⁵⁷Fe Mössbauer analysis. For both nucleophiles a single major species was generated with parameters $\delta = 0.3$ mms⁻¹ and $E_Q = 1.10$ mms⁻¹. This result demonstrates the negligible effect in the choice of the nucleophile cation on the nature of the generated iron product. Similarly, a reaction aliquot was taken from both reactions and freeze-trapped for analysis using EPR spectroscopy. The resultant spectrum displays intense features around $g \sim 4.3$, indicative of the generation of $S = 5/2$ iron-species, consistent with a distorted tetrahedral iron(III) complex. Combined with the observed single Mössbauer species, the broadness of the EPR features is consistent with small changes in the iron coordination environment, such as varying association of the lithium cation to the second-sphere coordination environment around the iron center, possibly adopting a distal ion-pair type dynamic (i.e. forming Li(THF)₄). Through monitoring of the in situ iron speciation, the complex was also found to be stable in solution over hours.

Encouraged by the formation of a $S = 5/2$ iron species in these reactions and its relative stability in solution, extensive crystallization efforts were pursued in order to isolate and structurally characterize the iron product of these reactions. While reactions with both nucleophiles were pursued, the organolithium reagent reactions enabled the generation of crystalline material. Similar to the reaction protocol utilized for obtaining the Mössbauer spectra, Fe(acac)₃ was dissolved in THF, cooled to -78 °C and 5 equiv of LiCH₂TMS were added in one portion. After allowing the reaction to stir at RT for 5 min, the resultant orange colored solution was cooled back to -78 °C, cold pentane was added, and the reaction was stored at -80 °C for several days. Orange single crystals suitable for X-ray diffraction were obtained and the structure was determined to be the distorted tetrahedral complex, [Li(THF)₂][Fe(CH₂Si(CH₃)₃)₄] (**1**) (τ_4 parameter of 0.94) consistent with the parameters seen by EPR and Mössbauer.³¹ The Fe-CH₂ bond lengths range from 2.0712(14) to 2.1318(14) Å. Upon comparison of **1** with the previously reported complexes [FeBn₄]⁻ and [FeMe₄]⁻ (2.081(2) to 2.101(2) and 2.009(14) to 2.051(13) Å, respectively), the similarity of the bond lengths of **1** and [FeBn₄]⁻ are consistent with the apparent similarities in their overall electronic structures. However, the broad range of Fe-CH₂ bond lengths in **1** reflects lithium cation interaction, which appears necessary for the stabilization of the complex. Importantly, ligation of THF to the lithium cation also appears to be essential for successful formation of **1**. This was tested using only pentane as the reaction solvent which led to intractable reaction mixtures.

Similar effects of lithium nucleophiles were reported by Fürstner where coordination of the lithium to the alkyl substituents in the iron's second coordination sphere greatly stabilized the homoleptic alkyl iron complexes and allowed for their isolation and characterization.^{17,20} The Fe(II) complex, [Li(OEt₂)]₂[(Me₄Fe)(MeLi)], displayed a broad range of Fe-CH₃ bond lengths due to the coordination of lithium cations (2.095(4) to 2.188(4) Å) which

exhibited an even larger range than that of **1**. While it was previously demonstrated that significant changes in coordination geometry and a change in oxidation state of homoleptic iron-methyl complexes could be accomplished by changing the nature of the methyl nucleophile ($[\text{FeMe}_4]^-$ formed with MeMgBr whereas $[\text{FeMe}_4]^{2-}$ is formed with MeLi), analogous effects do not appear to occur for reactions involving trimethylsilylmethyl nucleophiles as the same species is formed in situ with either TMSCH_2Li or $\text{TMSCH}_2\text{MgCl}$ as determined by Mössbauer (vide supra).

Spin-unrestricted DFT was utilized to reveal detailed information on the electronic structure and bonding of **1**. The hybrid functional, B3LYP, and a def2-TZVP basis set were utilized for geometry optimization. The bis-THF lithium cation was included in all calculations due to its close coordination to the methylene centers. Good agreement between calculated and experimental bond lengths and angles was obtained (Table 1) and allowed for further evaluation of the electronic structure through single point calculations. The ground-state electronic structure of **1** can best be described from the examination of the frontier molecular orbitals of the β -manifold (Figure 4). As expected for a $S = 5/2$ iron(III) system, the most d-orbital character was determined to be present in the lowest unoccupied molecular orbitals energy orbital, $\beta 155$, determined to be the d_z^2 orbital. It should be noted that d-orbitals $\beta 153$ and $\beta 154$ (d_{xz} and d_{xy}) are close in energy (differ by only 0.01 eV). Modest antibonding interactions are present in two of the LUMOs, $\beta 153$ and $\beta 154$, while distinct interactions between the methylene ($-\text{CH}_2-$) and iron d-orbitals were observed in three HOMOs with σ -bonding ($\beta 148$ –150).

Further insight into the metal-ligand bonding in **1** was obtained through evaluation of the Mayer bond orders (MBO) and charge donation analysis. The Fe- CH_2 bond-lengthening effect of the lithium cation coordination observed in the crystal structure was reinforced in the calculated parameters. A decrease in MBOs of both Fe-C9 and Fe-C13 (0.610 and 0.624, respectively) compared with Fe-C1 and Fe-C5 bonds demonstrated the extent of this lithium coordination effect. Charge donation analyses revealed a significant total $\text{L} \rightarrow \text{Fe}$ donation of $3.264 e^-$ from the α - and β -manifold (α and β). As expected, the total net donation to the fully unoccupied iron(III) β -manifold $[\text{Fe}(\text{CH}_2\text{TMS})_4]^-$ is significantly greater ($1.412 e^-$ compared to $0.656 e^-$) than that of the fully occupied α -manifold. As predicted the $-\text{CH}_2\text{TMS}$ ligand results in a substantially larger charge donation effect for **1** compared with the analogous methyl and benzyl complexes (2.429 and $2.463 e^-$, respectively). Despite this increased donation, **1** retains a distorted tetrahedral geometry as a result of ligand steric effects. Combined with previous studies for $[\text{Fe}(\text{Bn})_4]^-$, this result indicates the significant importance of steric effects in determining structure in homoleptic tetraalkyliron(III) complexes.

Moving forward, studies of alkyl ligands that have limited steric bulk yet are poor donor ligands will be of interest in order to further define these contributions in tetraalkyliron(III) complexes. The CF_3 analog of complex **1** is of particular interest due to the possibility of an electron deficient tetraalkyl complex which due to the decrease in charge donation might adopt a tetrahedral geometry even in the presence of limited ligand steric bulk. This hypothesis is consistent with the overall tetrahedral environment adopted by $[\text{Li}(\text{OEt}_2)_2][(\text{Me}_4\text{Fe})(\text{MeLi})]$ due to the decrease in electron donation of the CH_3 from

lithium coordination, although it should be noted that this complex is in the 2+ oxidation state as opposed to the 3+ of the other examples. However, this complex exhibits significant steric bulk, a characteristic consistent with **1** and $[\text{FeBn}_4]^-$, from the closely associated solvent and cations which would also favor the tetrahedral geometry. A full evaluation of the electronic structure of an electron deficient homoleptic iron(III) ferrate (such as $[\text{Fe}(\text{CF}_3)_4]^-$) with a distal counter-ion would help to elucidate whether electronic or steric effects have the stronger influence on the overall coordination geometry and spin-state.

Lastly, in light of the structural perturbation of **1** resulting from close Li cation interactions, it is interesting to note that the in situ Mössbauer spectra of **1** formed with either TMSCH_2Li or $\text{TMSCH}_2\text{MgCl}$ are identical. Although adoption of a completely different coordination geometry was not expected by changing the nucleophile cations, our previous studies involving magnesium counterions have demonstrated a strong preference for the formation of distal coordination spheres which behave as close ion pairs. However, the lack of change in spectral parameters from Mössbauer suggests that either magnesium directly takes the place of Li in the coordination sphere around the iron (likely as MgX ; $\text{X} = \text{acac}$ or Cl) or in solution there are no close cation interactions to perturb the iron-alkyl bonding. It seems unlikely that the dissociation of this lithium cation (perhaps to form $\text{Li}(\text{THF})_4$) would not influence the overall electron density as the bond lengths of the coordinating methylene centers are elongated from the close contact of the lithium and which is consistent with the distortions that were observed from EPR.

4. Conclusion

In the current study, a new tetraalkyliron(III) complex has been prepared that contains trimethylsilylmethyl ligands that both increase alkyl ligand donor strength while retaining steric bulk, providing a system to further evaluate the relative contributions of these effects on structure and bonding in tetraalkyliron(III) complexes. Detailed structural and DFT studies provide insight into electronic structure and bonding of this distorted tetrahedral complex compared to the analogous methyl (distorted square planar) and benzyl (distorted tetrahedral) complexes. Overall, these results demonstrate that increased charge donation from stronger electron-donor ligands which contain increased steric bulk relative to methyl ligands has a limited effect on the resultant coordination geometry. The insight into alkyl ligand effects on electronic structure and bonding defined provide a critical basis for understanding the effects of alkyl nucleophile variations on the nature and stability of iron-alkyl complexes of relevance to iron-catalyzed cross-coupling. Further studies of homoleptic organoiron(III) complexes formed using a broader range of alkyl, alkenyl and aryl nucleophiles will be critical to developing a molecular level understanding of nucleophile-derived ligand effects on organoiron(III) species in iron-catalyzed cross-coupling reactions utilizing simple ferric salts.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

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Fig. 1.
 $[\text{FeMe}_4]^-$ and $[\text{FeBn}_4]^-$ complexes reported by Neidig [1] and Bedford [21], respectively.

Figure 2.

A) 80 K ^{57}Fe Mössbauer spectrum of a frozen solution of $^{57}\text{Fe}(\text{acac})_3$ with 5 equiv of $\text{TMSCH}_2\text{MgCl}$ in THF at RT (black dots), total fit (red trace). B) 80 K ^{57}Fe Mössbauer spectrum of a frozen solution of $^{57}\text{Fe}(\text{acac})_3$ with 5 equiv of TMSCH_2Li in THF at RT (black dots), total fit (red trace). The 10 K EPR spectra of frozen solutions of the reaction of $^{57}\text{Fe}(\text{acac})_3$ with 5 equiv of $\text{TMSCH}_2\text{MgCl}$ (2A, inset) and TMSCH_2Li (2B, inset) in THF at RT.

Figure 3. Synthesis of [Li(THF)₂][Fe(CH₂Si(CH₃)₃)₄] (**1**). Structure of **1**, drawn at 50% probability level. Hydrogen atoms omitted for clarity. Note: Only one of two crystallographically-independent molecules of the asymmetric unit are displayed.

Figure 4.

Calculated molecular orbital diagram for **1**. *Note that MO $\beta 154$ is only 0.01 eV higher in energy than $\beta 153$.

(LUMOs). The LUMOs ($\beta 151$, $\beta 152$, $\beta 153$, $\beta 154$, and $\beta 155$) contain significant d-orbital character with the highest

Table 1.

Calculated vs. Experimental Bond Lengths and Angles for 1

	Exptl	Calcd
Fe-C1	2.0746 Å	2.0927 Å
Fe-C5	2.1317 Å	2.1703 Å
Fe-C9	2.0712 Å	2.0986 Å
Fe-C13	2.1170 Å	2.1686 Å
C5-Fe-C13	104.13°	103.74°
C5-Fe-C9	109.08°	109.87°