Quantitation of the THF Content in Fe[N(SiMe₃)₂]₂·xTHF

Daniël L. J. Broere, Ilija Ćorić,[†] Anna Brosnahan, and Patrick L. Holland*[ORCID]

Department of Chemistry, Yale University, 225 Prospect Street, New Haven, Connecticut 06520, United States

S *Supporting Information*

ABSTRACT: The absence of residual solvent in metal precursors can be of key importance for the successful preparation of metal complexes or materials. Herein, we describe methods for the quantitation of residual coordinated tetrahydrofuran (THF) that binds to Fe[N-(SiMe₃)₂]₂, a commonly used iron synthon, when prepared according to common literature procedures. A simple method for quantitation of the amount of residual coordinated THF using ^{1}H NMR spectroscopy is highlighted. Finally, a detailed synthetic procedure is described for the synthesis of THF-free Fe[N(SiMe₃)₂]₂.

The presence or absence of residual (coordinated) solvent in metal precursors is important when preparing complexes for the coordination of weakly binding ligands like N_2 or H_2 and in the synthesis of colloidal inorganic nanocrystals and nanoparticles.[1] One series of metal precursors that has gained popularity in both fields is metal bis(trimethylsilyl)amides, which were first studied by Bürger and Wannagat[2] and popularized by Bradley et al.[3] The high lipophilicity of these compounds is evident from their solubility in alkanes and other nonpolar solvents.[4] This feature, in combination with an internal base (which is protonated to give a volatile and soluble conjugate acid), makes them attractive alternatives to metal halides as metal precursors in organometallic chemistry[5] as well as in the preparation of nanomaterials.[6]

In this paper, we address Fe[N(SiMe₃)₂]₂ (Scheme 1), which has been used in more than 150 papers as a starting material. This

Scheme 1. Monomer–Dimer Equilibrium of Fe[N(SiMe₃)₂]₂ in Solution, Where $K_{eq} = 5 \times 10^{-3}$ at 300 K[8]
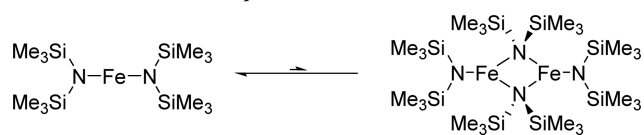
compound can be isolated as a green liquid after distillation under reduced pressure and was first described by Andersen et al. in 1988.[7] As with other metal bis(trimethylsilyl)amides, the reported synthetic procedure involves a reaction of the metal halide solvate FeBr₂(THF)₂ (THF = tetrahydrofuran) with 2 mol equiv of LiN(SiMe₃)₂ in Et₂O. The product was structurally characterized in the gas phase as a solvent-free two-coordinate iron amide,[7] but no elemental analysis was provided. In 1991, Power et al. reported the characterization of Fe[N(SiMe₃)₂]₂ in solution and the solid state as well as the isolation of its THF adduct Fe[N(SiMe₃)₂]₂(THF) when using THF as the reaction

solvent instead of Et₂O.[8] At ambient temperature, Fe[N-(SiMe₃)₂]₂ exists as a linear monomer in the solution and gas phases, but it dimerizes in the solid state or at lower temperatures in solution (Scheme 1).

Although most of the >170 publications[9] cite the work of Andersen et al. for the synthesis of Fe[N(SiMe₃)₂]₂, in our hands the reported synthetic procedure yielded samples containing variable amounts of THF after distillation, even when the preparative method did not use THF as a solvent.[10] The need for accurate knowledge of the iron content, and the desire to have a robust and easy spectroscopic gauge for the THF content, encouraged us to investigate the characterization of Fe[N-(SiMe₃)₂]₂ in more detail. Herein, we detail our findings on the THF content of Fe[N(SiMe₃)₂]₂ samples when prepared according to literature procedures, as well as an alternative synthetic procedure that yields THF-free Fe[N(SiMe₃)₂]₂.[11] In addition to elemental analysis, we use several different methods for quantifying the amount of THF in the product, culminating in a ^{1}H NMR measure of the THF content that is simple to use on an everyday basis. These systematic studies should be of use to the research community that uses this convenient starting material.

The reaction of FeBr₂(THF)₂ with 2 equiv of LiN(SiMe₃)₂ in Et₂O, according to the procedure reported by Andersen et al., yielded a green oil after purification by distillation, and it solidified upon cooling as reported.[7] However, ^{1}H NMR analysis in C₆D₆ of the product showed not only the expected broad resonance for the SiMe₃ protons but also two additional broad resonances. The material was characterized as Fe[N-(SiMe₃)₂]₂(THF)₀.₄₇ (see below), which was surprising because the final purification step is a distillation under reduced pressure, and the only THF present in the synthesis was part of the starting material FeBr₂(THF)₂. The amount of THF was tentatively quantified using ^{1}H NMR integrations of the resonances for natural abundance THF, which appear next to the residual solvent (THF-d_7) peaks in a THF-d_8 solution (see the Supporting Information). The NMR spectra of samples of this material in both C₆D₆ and THF-d_8 have a broad peak corresponding to the SiMe₃ protons, implying that exchange of the coordinated THF between Fe[N(SiMe₃)₂]₂(THF) and Fe[N(SiMe₃)₂]₂ is fast on the NMR time scale in solution. The presence of two distinct iron species in the isolated material was confirmed by Mössbauer spectroscopy of a solid sample at 80 K, and the stoichiometry Fe[N(SiMe₃)₂]₂(THF)₀.₄₇ (as determined by ^{1}H NMR analysis) agreed very well with the 52:48 ratio of the intensities of two doublets in the Mössbauer spectrum (Figure 1, top). To confirm the identity of the THF
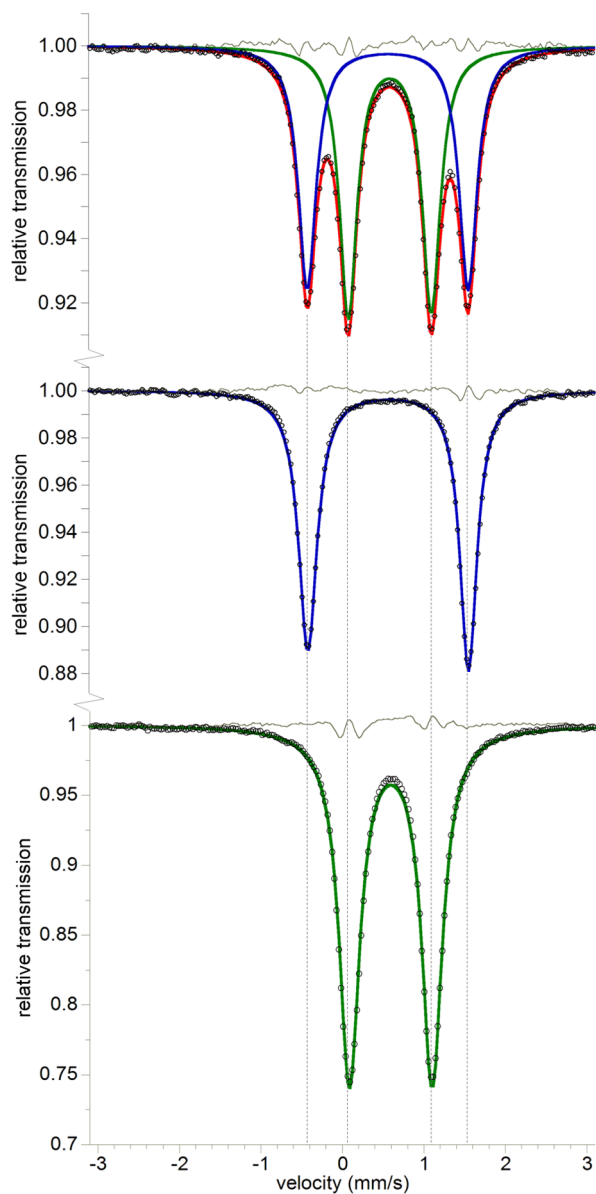
Figure 1. Zero-field Mössbauer spectra (80 K). Top: Fe[N-(SiMe$_3$)$_2$]$_2$(THF)$_{0.47}$ (green line, δ = 0.60 mm/s and $|\Delta E_Q|$ = 1.02 mm/s, 52%; blue line, δ = 0.57 mm/s and $|\Delta E_Q|$ = 1.97 mm/s, 48%). Middle: Fe[N(SiMe$_3$)$_2$]$_2$(THF)$_{1.03}$ (δ = 0.57 mm/s and $|\Delta E_Q|$ = 1.97 mm/s). Bottom: Fe[N(SiMe$_3$)$_2$]$_2$ (δ = 0.59 mm/s and $|\Delta E_Q|$ = 1.02 mm/s). The black circles are the data, the colored lines are the simulations, and the gray lines are the residuals.

adduct, an excess of THF was added to light-green Fe[N-(SiMe$_3$)$_2$]$_2$(THF)$_{0.47}$, resulting in a nearly colorless solution. Drying under vacuum provided the bona fide THF adduct, as an almost colorless solid with a faint-blue hue.[12] Quantitation of the amount of THF in the product through integration of the ^{1}H NMR spectrum in THF-d_8 revealed the stoichiometry Fe[N-(SiMe$_3$)$_2$]$_2$(THF)$_{1.03}$, in agreement with coordination of a single molecule of THF. Moreover, the Mössbauer spectrum (Figure 1, middle) of this product revealed a doublet with identical isomer shift and quadrupole splitting as one of the doublets observed in the Mössbauer spectrum of Fe[N(SiMe$_3$)$_2$]$_2$(THF)$_{0.47}$ (Figure 1, top).

The observation of THF in the obtained product is curious as the reaction was performed in Et$_2$O as reported.[7] We surmise

that THF in the green product originated from the FeBr$_2$(THF)$_2$ starting material. Unfortunately, distillation is not effective for the separation of Fe[N(SiMe$_3$)$_2$]$_2$ from its THF adduct. Power et al. reported the fractional distillation of Fe[N(SiMe$_3$)$_2$]$_2$(THF) at temperature and pressure similar to those of its THF-free analogue and specifically noted that the metal bis(amide) retained the coordinated THF molecule throughout several distillations under reduced pressure and elevated temperature. In our hands, the procedure by Power et al. for the preparation of Fe[N(SiMe$_3$)$_2$]$_2$(THF) gives a product with ~0.9 equiv of THF. Redistillation gives partial loss of THF (to ~0.7 equiv). Hence, distillation is not a straightforward method for effecting the complete removal of coordinated THF.

Thus, we were interested in a robust procedure toward THF-free Fe[N(SiMe$_3$)$_2$]$_2$, ideally from commercially available materials that require no further purification. We found that using crushed anhydrous FeCl$_2$ beads in combination with LiN(SiMe$_3$)$_2$ (97% purity) in Et$_2$O enabled the isolation of Fe[N(SiMe$_3$)$_2$]$_2$ without THF.[11,13] Upon cooling of the highly air- and moisture-sensitive[14] green liquid after the distillation, a pale-green solid was obtained in 88% yield. ^{1}H NMR analysis in C$_6$D$_6$ revealed a single resonance at 65 ppm corresponding to the SiMe$_3$ protons. ^{1}H NMR analysis in THF-d_8 showed no THF resonances next to the solvent THF-d_7 peaks. Combustion elemental analysis of the pale-green solid was in good agreement with the calculated values for Fe[N(SiMe$_3$)$_2$]$_2$. Finally, the Mössbauer spectrum (Figure 1, bottom) of this product revealed a doublet with nearly identical isomer shift and quadrupole splitting as one of the doublets observed in the Mössbauer spectrum of Fe[N(SiMe$_3$)$_2$]$_2$(THF)$_{0.47}$ (Figure 1, top).

Because few laboratories are equipped with a Mössbauer spectrometer or facilities to perform elemental analysis of highly sensitive compounds and because THF-d_8 is expensive, we sought methods to easily determine the THF content in a Fe[N(SiMe$_3$)$_2$]$_2$ sample. There is a color difference between Fe[N(SiMe$_3$)$_2$]$_2$ (light green) and Fe[N(SiMe$_3$)$_2$]$_2$(THF) (faint blue), and when we performed a UV−vis titration by adding known substoichiometric amounts of THF to a solution of Fe[N(SiMe$_3$)$_2$]$_2$ in heptane (see Supporting Information), a subtle blue shift and a decrease in the intensity of a weak absorption band in the visible region were observed along with the appearance of a new weak absorption band in the near-IR. However, this is not an ideal quantitation method because of the low extinction coefficients and because of intensely colored impurities that can form upon exposure to traces of air or moisture.

We observed that the chemical shift of the SiMe$_3$ protons in the ^{1}H NMR spectrum in C$_6$D$_6$ varied greatly for samples with varying THF content, which we attribute to the rapid exchange of THF on the NMR time scale. With the THF-free Fe[N-(SiMe$_3$)$_2$]$_2$ in hand, we performed an NMR titration by adding known substoichiometric amounts of THF to a solution of Fe[N(SiMe$_3$)$_2$]$_2$ in C$_6$D$_6$ at 295 K. A linear relationship was observed between the amount of THF equivalents and the chemical shift of the SiMe$_3$ resonance, which shifts upfield with increasing THF content (Figure 2). Thus, the bound THF is in fast exchange on the NMR time scale. After the addition of more than 1 equiv of THF, no further change in the chemical shift of the SiMe$_3$ protons is observed. The chemical shifts of the SiMe$_3$ resonances in ^{1}H NMR spectra of other samples with known THF content (determined through integration in THF-d_8) agreed with the equation depicted in Figure 2, regardless of their concentration. Therefore, we recommend that this equation be
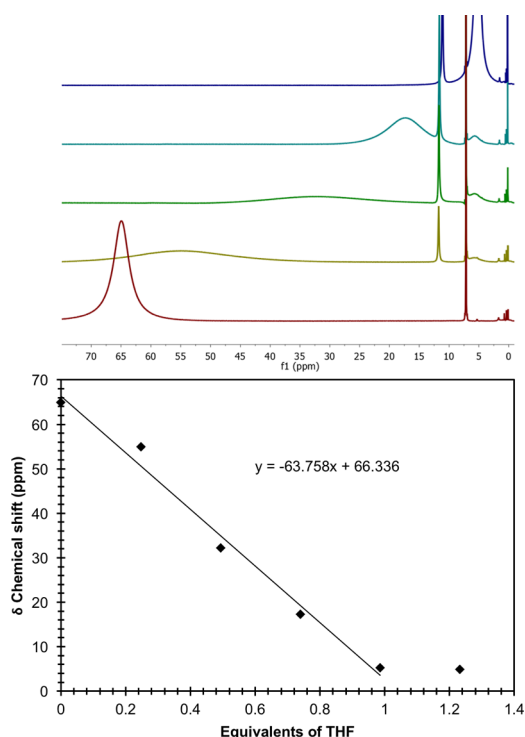
Figure 2. Top: Stacked ^1H NMR spectra of $Fe[N(SiMe_3)_2]_2(THF)_x$ in C_6D_6 at 295 K showing the spectral changes upon increasing amounts of THF equivalents. Bottom: Plot of the chemical shift of the $SiMe_3$ protons in $Fe[N(SiMe_3)_2]_2(THF)_x$ versus the amount of THF.

used as a routine method for determining the THF content in samples of $Fe[N(SiMe_3)_2]_2(THF)_x$ ($x = 0-1$). When this equation is used, it is important that the samples are at 295 K because the chemical shifts of the peaks for paramagnetic compounds have a strong temperature dependence.

To gain additional verification of the stoichiometry of THF binding in solution, we used the method of continuous variation (Job's method).[15,16] The Job plot shows a maximum at a mole fraction of 0.5, confirming the 1:1 stoichiometry of THF binding in C_6D_6 at 295 K (Figure 3). Both the abrupt halt in the chemical shift change of the $SiMe_3$ protons after the addition of more than 1 equiv of THF, and the sharp peak in the Job plot, are indicative of very strong binding ($K_a > 1000$).[14,17]
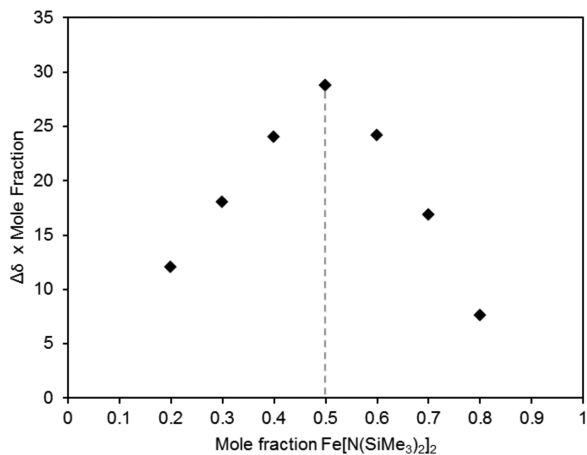
Figure 3. Job plot showing the 1:1 stoichiometry of THF binding to $Fe[N(SiMe_3)_2]_2$ in C_6D_6. $[THF] + [Fe[N(SiMe_3)_2]_2] = 132$ mM.

In conclusion, the preparation of $Fe[N(SiMe_3)_2]_2$ according to its literature procedure from $FeBr_2(THF)_2$[7] can result in a product containing residual coordinated THF. The best way to obtain THF-free $Fe[N(SiMe_3)_2]_2$ is to make sure that it is never exposed to THF.[11,13] Because even THF from the $FeBr_2(THF)_2$ precursor is partially retained after vacuum distillation, we report alternative procedures using commercially available starting materials to prepare THF-free $Fe[N(SiMe_3)_2]_2$ and $Fe[N-(SiMe_3)_2]_2(THF)$. Four complementary methods for quantification of the THF content are described (elemental analysis, Mössbauer spectroscopy, ^1H NMR in THF-d_8, and ^1H NMR in C_6D_6), and the last of these methods is most convenient in the everyday characterization of the THF content in samples of $Fe[N(SiMe_3)_2]_2(THF)_x$.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b00056.

Experimental procedures, spectra, and photographs (PDF)

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: patrick.holland@yale.edu.

ORCID ⓞ
Patrick L. Holland: 0000-0002-2883-2031

Present Address
†I.Č.: Department of Chemistry, University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland.

Notes
The authors declare no competing financial interest.

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(12) The addition of an excess of THF to a sample of Fe[N(SiMe$_3$)$_2$]$_2$ with any amount of coordinated THF, followed by extensive drying in vacuum at room temperature, affords bona fide Fe[N(SiMe$_3$)$_2$]$_2$(THF). See the Supporting Information for more details.

(13) Experimental procedure for Fe[N(SiMe$_3$)$_2$]$_2$: Inside a N$_2$-filled glovebox, a Schlenk flask was charged with crushed anhydrous FeCl$_2$ beads (3.80 g, 30.0 mmol) and Et$_2$O (120 mL). The stirred suspension was cooled to 0 °C, after which a solution of LiN(SiMe$_3$)$_2$ (10.0 g, 60.0 mmol) in Et$_2$O (180 mL) was added dropwise (∼3 drops/s). The suspension was allowed to warm slowly to ambient temperature and was stirred for 20 h. Volatile materials were removed under vacuum, and the dark-green residue was extracted with pentane (3 × 25 mL). The dark-green extracts were filtered, transferred into a round-bottom Schlenk flask, and concentrated under vacuum to a dark-green oil. The Schlenk flask was connected to a distillation apparatus, and the oil was distilled under reduced pressure (30 mTorr) to afford a pyrophoric green oil at 80−90 °C (sole fraction; oil bath temperature 105−110 °C). The product was directly transferred into a N$_2$-filled glovebox, and the oil solidified upon cooling to afford a light-green solid (9.9 g, 88% yield). ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 64.9 (36H, broad). Anal. Calcd for C$_{12}$H$_{36}$FeN$_2$Si$_4$: C, 38.27; H, 9.64; N, 7.44. Found: C, 38.30; H, 9.82; N, 7.62. Similar procedures are given in refs 11a and 11b.

(14) Upon exposure to air or water, a rapid exothermic reaction occurs that can result in spontaneous combustion of the material when handled in large amounts. Therefore, great care should be exercised during the use and distillation of Fe[N(SiMe$_3$)$_2$]$_2$. See the Supporting Information for photographs and a further description of the synthetic procedures.

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