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Mössbauer spectroscopic and computational investigation of an iron cyclopentadienone complex.

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(cyclopentadienone)iron carbonyl complexes • Mössbauer spectroscopy • computational study •
chemical activation • iron catalysis.

ABSTRACT.

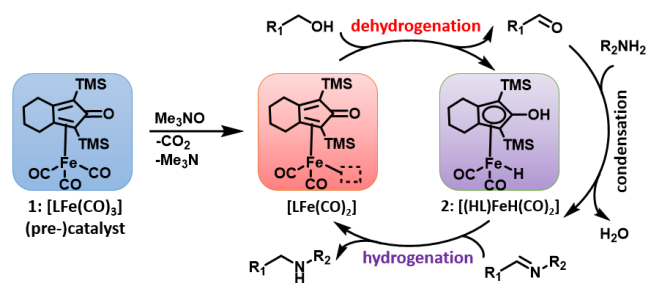
(cyclopentadienone)iron carbonyl complexes have recently received particular attention in their use as catalysts for hydrogenation or transfer hydrogenation reactions including the *N*-alkylation of amines with alcohols. This is due to their easy synthesis from simple and cheap materials, air and water stabilities, and to the crucial metal-ligand cooperation giving rise to unique catalytic properties. Here, we report a Mössbauer spectroscopic and computational investigation of such a complex and of its corresponding activated species prompt for dehydrogenation and hydrogenation reactions. This study affords a deeper understanding on the species formed upon reaction with Me₃NO and on their distribution upon the added amount of oxidant.

INTRODUCTION.

The direct catalytic high atom economy and sustainable *N*-alkylation of amine with alcohol through borrowing hydrogen catalysis is considered as one of the most promising methods to access sustainably valuable pharmaceutical ingredients containing amine groups from readily available stable alcohols. For decades, this field has endured dominance of late and mostly noble metal based homogeneous¹ and heterogeneous² catalysts. Recently, the development of efficient molecular catalysts based on non-precious, non-toxic and earth abundant metal such as iron encompassed growing interest.³ Among these catalysts, (cyclopentadienone)iron carbonyl complexes ([LFe(CO)₃], further denoted **1**) hold a special place due to their easy synthesis from simple and cheap materials, their air and water stability and to the metal-ligand cooperation giving rise to unique catalytic properties.⁴ The proposed mechanism proceeds as following: the pre-catalyst **1** is thermally, photochemically and/or chemically activated via CO decoordination (Scheme 1). It is proposed to lead to the formation of the corresponding complex [LFe(CO)₂]

that is prompt to dehydrogenate the alcohol forming an activated carbonyl intermediate.⁵ The resulting dihydrogen is temporarily stored on the molecular catalyst. A subsequent condensation with the amine forms an imine, which then undergoes hydrogen transfer by the complex $[(HL)FeH(CO)_2]$ (further denoted **2**) to give the *N*-alkylated product with regeneration of the active iron complex. The overall process is hydrogen and redox neutral and produces water as the only stoichiometric by-product. Consequently, this catalytic domino process allows considerable step, waste and atom economies compared to traditional sequential reactions. As such, it offers a ground-breaking eco-compatible methodology for C-N bond formation. Another advantage of these catalysts lies in the fact that the use of a strong external base such as KO^tBu is not required to obtain an efficient catalytic system compared to what is done with numerous pincer type complexes for instance. As such, they are considered as base free catalytic systems. Note that it does not exclude the possibility of the amine substrate to act possibly as a base. The first iron-cyclopentadienone catalyzed *N*-alkylation of amine with alcohol was reported in 2014 by Barta and collaborators⁵ followed by numerous other examples.^{6–8} and references therein

Scheme 1. *N*-alkylation of amine with alcohol catalyzed by (cyclopentadienone)iron carbonyl complex.



Given this reactivity, (cyclopentadienone)iron carbonyl complexes are able to catalyze diverse reactions including the hydrogenation or transfer hydrogenation of carbonyl and imine

compounds, the direct amination of carbonyl compounds and the hydrogenolysis of esters to alcohols to name a few.^{4,6-8} Usually, an outer-sphere mechanism is proposed for these hydrogenation reactions with two key intermediates named $[\text{LFe}(\text{CO})_2]$ and **2** as for the *N*-alkylation of amines. It may be noticed that conversely to **2** that has been isolated and characterized, $[\text{LFe}(\text{CO})_2]$ has never been isolated and no spectroscopic signatures have been reported so far.

Among the different activation modes to generate $[\text{LFe}(\text{CO})_2]$ active for dehydrogenation reactions, the convenient use of a chemical activator such as Me_3NO accounts for the most employed methodology in the literature.⁶⁻⁸ and references therein In principle, one equivalent of trimethylamine-*N*-oxide is sufficient to convert stoichiometrically **1** into $[\text{LFe}(\text{CO})_2]$. However, varying amounts of Me_3NO from one up to several equivalents are used to activate the precatalyst. We anticipate that the ratio pre-catalyst/ Me_3NO may influence the distribution and the type of species formed upon activation of the precatalyst. Herein we report a Mössbauer spectroscopic investigation of the precatalyst **1** and its corresponding active species, in combination with quantum chemistry. We address the effect of the quantity of Me_3NO used in respect to **1** on the distribution of the iron species formed during the course of CO decoordination. We will show here that spectroscopic and computational studies support the formation of trimethylamine containing complexes. This questions the adage considering the (cyclopentadienone)iron carbonyl as a base free catalytic system.

EXPERIMENTAL SECTION

General. All manipulations were performed under an atmosphere of purified argon using standard Schlenk and glove-box techniques. Anhydrous toluene (Sigma Aldrich, ACS reagent)

was used as received. CDCl_3 (Eurisotop) was pass through a short pad of neutral alumina prior to use. $[\text{FeL}(\text{CO})_3]^{9,10}$ and $[(\text{HL})\text{FeH}(\text{CO})_3]^{11}$ were prepared according to published procedures.

Instrumentation. ^1H and ^{13}C -NMR spectra were recorded at 400 MHz on a Varian Avance III 400 spectrometer. UV-visible spectra were obtained with a Hewlett Packard HP 89090A spectrometer. Mössbauer spectra were recorded on powder samples or on toluene solutions contained in Delrin cups of natural-abundance ^{57}Fe compounds (iron complexes at 22mM). Mössbauer spectra were recorded at 80 K on a low-field Mössbauer spectrometer equipped with a Janis SVT 400 cryostat or on a strong-field Mössbauer spectrometer equipped with an Oxford Instruments Spectromag 4000 cryostat containing a 8 T split-pair superconducting magnet. The spectrometer was operated in a constant acceleration mode in transmission geometry. All velocity scales and isomer shifts are referred to the metallic iron standard at room temperature. Analysis of the data was performed with a homemade program.^{12,13} Full experimental details including samples preparation, spectroscopic (^1H and ^{13}C NMR, Mössbauer) and details of computational calculations are given in the Supporting Information.

Computational Details. Geometry optimizations and Mössbauer parameters calculations were carried out using the ORCA program, version 3.0.3.¹⁴ Geometry optimizations of all compounds were performed at the TPSSh¹⁵ level of theory (employing the RIJCOSX approximation^{16,17}), including the ZORA scalar relativistic method^{18,19}, relativistically recontracted versions of the Karlsruhe def2-TZVP basis sets^{20,21} and D3-dispersion correction.^{22,23} Solvation effects were accounted for using the Conductor-like Screening Model (COSMO).²⁴ Geometry optimization was followed by a frequency calculation to obtain the Gibbs energy (taken as the sum of electronic and thermal free energies). Single-point calculations were performed using the hybrid GGA functional B3LYP (20% HF exchange) to obtain electron-density values at the Fe nuclear

positions that were used to derive the isomer shifts. A mixed basis set was used that consists of the core-polarized CP(PPP) basis set^{25,26} on Fe atoms and DKH-def2-TZVP^{20,21} on all other atoms. Scalar relativistic effects in the Mössbauer isomer shift calculations were accounted for using the second-order Douglas–Kroll–Hess approximation. The ⁵⁷Fe Mössbauer isomer shifts were calibrated using the extended (“whole”) calibration parameters according to Neese,²⁷ which includes previously reported^{28,29} calibration sets. $\delta_{\text{iso}} = \alpha(\rho_0 - C) + \beta$, with: $\alpha = -0.173830492$, $\beta = 0.37718458$ and $C = 23615$. ¹³C NMR chemical shift values were computed using the gauge-independent atomic orbital (GIAO) method incorporated^{30,31} into Orca 4.21,³² the B3LYP functional, and the relativistically recontracted versions of the Karlsruhe def2-TZVP basis sets^{20,21} were used. Isotropic shielding values obtained from the computation were referenced to the carbon isotropic shielding values of tetramethylsilane (TMS) computed at the same level of theory.

RESULTS

Mössbauer spectroscopy. Most of the *N*-alkylation of amine with alcohol reactions involving **1** and **2** have been performed in toluene.^{6–8} and references therein ⁵⁷Fe-Mössbauer spectroscopy is sensitive to the electron density on the iron site, and therefore to changes in the coordination sphere. This prompted us to investigate the frozen toluene solutions of these complexes by Mössbauer spectroscopy. Because the concentration can be as high as 50 mM, no enrichment in ⁵⁷Fe was required. Both complexes were synthesized according to previously published procedures.^{9–11} Spectra *a* and *b* in Figure 1 correspond to the 80 K and zero-field spectra of **2** and **1**, respectively. Both species are characterized by a doublet. The Mössbauer parameters are listed in Table 1. The isomer shift for the hydride complex **2** is slightly smaller than that of the tricarbonyl species **1** (0.02 and 0.06 mm s⁻¹, respectively) whereas the reverse order is

determined for the quadrupole splitting values (1.72 and 1.49 mm s⁻¹, respectively). The Mössbauer nuclear parameters for **1** in frozen solution are similar to those determined at 80 K on a powder sample ($\delta = 0.06$ mm s⁻¹ and $\Delta E_Q = 1.47$ mm s⁻¹, see Figure S1), indicating that the structure is retained upon dissolution in toluene. Measurements at 5 K on both the solid and the toluene solution demonstrate the diamagnetic character of **1** (see Figure S1 and Table S1).

We then turned to the investigation of the mode of action of trimethylamine-*N*-oxide on **1**. Three different solutions were studied, generated by adding 1, 2 and 4 equivalents of Me₃NO at room temperature. UV-visible monitoring evidenced completion of the reactions after 10 minutes (see Figure S2). Mössbauer spectra of the corresponding frozen solutions are reproduced in Figure 1 (see spectra *c-e*). The comparison with spectrum *b* clearly evidenced that the starting complex is still present in solutions with 1 and 2 equiv of Me₃NO. A second iron site characterized by a doublet with lines at ≈ -0.35 and $\approx +0.75$ mm s⁻¹, is identified in spectrum *c* that became the major component in spectrum *d*. A perusal of this series of four spectra also allows to evidence a third doublet with the low and high velocity lines located at ≈ 0.0 and ≈ 1.1 mm s⁻¹, respectively. Accordingly, spectra *c-e* were simultaneously simulated considering three doublets, one being that of **1** previously determined from spectrum *b*, the other two being labeled **3** and **4**. The result is shown in Figure 1 as bold solid lines overlaid on the experimental spectra. Parameters are listed in Table 1.

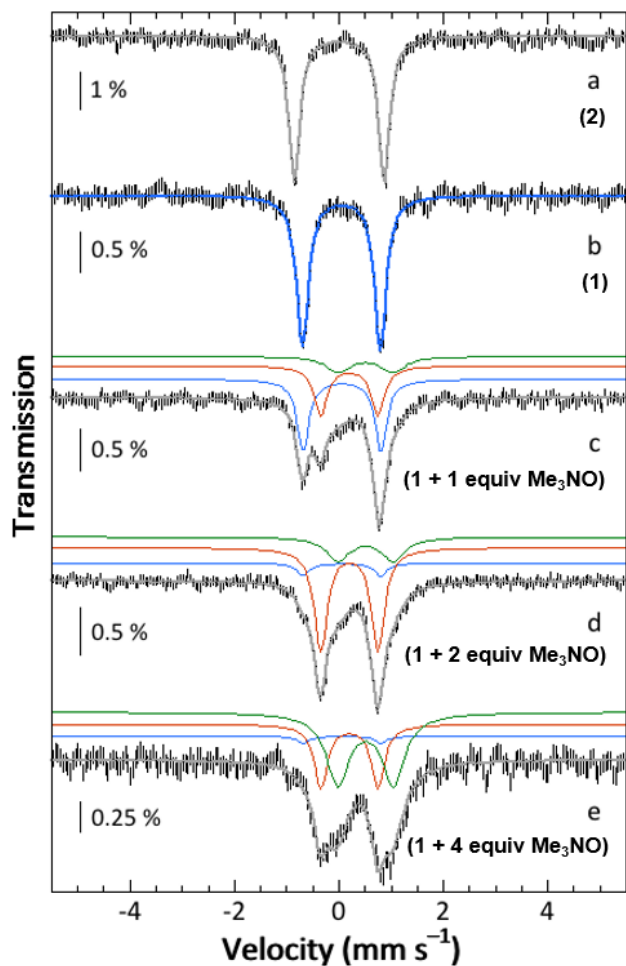


Figure 1. 80 K and zero-field Mössbauer spectra (hatched bars) of frozen toluene solutions of **2** (a), **1** (b), **1** + n equiv Me_3NO ($n=1$ (c); $n=2$ (d); $n=4$ (e)). Spectrum *a* was corrected from the contribution (12 %) of an impurity ($\delta=0.26 \text{ mm s}^{-1}$, $\Delta E_Q=1.87 \text{ mm s}^{-1}$). Simulations are shown as grey solid lines, except for spectrum *b*. Deconvolution is shown above spectra *c-e* with the color code: **1** in blue; **3** in red; **4** in green. See Table 1 for parameters.

Table 1. Mössbauer parameters determined from simulations of spectra *a-e*. Only the absolute value of the quadrupole splitting can be experimentally determined from zero-field Mössbauer spectra. Uncertainties are $\pm 0.02 \text{ mm s}^{-1}$, $\pm 0.05 \text{ mm s}^{-1}$, $\pm 0.02 \text{ mm s}^{-1}$, and $\pm 5 \%$ on δ , ΔE_Q , Γ_{fwhm}

and contribution, respectively. Values in parenthesis correspond to those determined by DFT calculations.

Solution	2	1 + n Me₃NO			
		<i>n</i>	1	3	4
δ (mm s ⁻¹)	0.02 (0.04)		0.06 (0.06)	0.20	0.51
ΔE_Q (mm s ⁻¹)	1.72 (1.92)		1.49 (1.49) ^[a]	1.09	1.06
Γ (mm s ⁻¹) ^[b]	0.25		0.28/0.27	0.31	0.54
Contribution (%)	100	0	100	0	0
		1	45	34	18
		2	8	71	28
		4	3	32	62

^a The close to 1 value determined for the η parameter (0.97, see SI) indicates that the sign of ΔE_Q is not relevant.

The linewidth for species **4** is significantly larger than that for **3**, suggesting a mixture of closely related structures for **4**, in contrast to a better-defined environment for the Fe site in **3**. The isomer shifts of species **3** and **4** generated upon action of Me₃NO are significantly larger than that of **1**, indicating successive and similar changes in the coordination sphere of the iron site. As anticipated, the starting complex **1** remains the major species (45 %) upon the addition of 1 equiv of Me₃NO whereas a drastic decrease to 8 % is observed upon reaction with 2 equiv. Only traces of **1** (3 %) are detected after the addition of 4. equiv. This Mössbauer study evidenced that more than one equivalent of Me₃NO are required for **3** to become the major species (34 % in spectrum *c*, 71 % in spectrum *d*) and that the addition of more than 2 equiv is detrimental (32 % in spectrum *e*). Concomitantly, **4** continuously increases upon the amount of added oxidant (18, 28, and 62 % in spectra *c-e*, respectively). Accordingly, it is tempting to identify species **3** as a key intermediate in dehydrogenation reaction.

DFT calculations. In order to provide a clear picture of the electronic structure of **1** and **2**, and to attempt to identify the species formed during the course of the reaction of the pre-catalyst with Me₃NO, a computational investigation was carried out using density functional theory (DFT). The calculations of the Mössbauer nuclear parameters closely follow a procedure developed by F. Neese and coworkers.^{27,28} Firstly, we focused on the isolated complexes **1** and **2**. Calculated coordination bond distances are over-estimated by 0.05 Å for **1**⁹ and 0.03 Å for **2**¹¹ compared to the X-ray data, as typically observed with current DFT functionals³³ (Figure S3, S4 and Table S2). Isomer shifts and quadrupole splittings derived from DFT calculations are displayed in Table 1. The agreement between experimental and theoretical values is very satisfying with deviations smaller than 0.02 and 0.20 mm s⁻¹ for δ and ΔE_Q , respectively. This comforted us in that calculating Mössbauer parameters will allow identifying the iron coordination spheres in **3** and **4**.

The reaction of the pre-catalyst with Me₃NO was proposed to release volatile CO₂ and Me₃N and accordingly form [LFe(CO)₂]. Early studies showed that the produced Me₃N can remain coordinated to transition-metal carbonyls complexes and that [(diene)Fe(CO)₂(NHMe₂)] can be produced while using at least two equivalents of Me₃NO.^{34,35} Thus, we considered the following series of complexes: [LFe(CO)₂], [LFe(CO)₂(NMe₃)] and [LFe(CO)₂(NHMe₂)]. For each complex, three conformational isomers were considered depending on the position of the released CO ligand (see Figure 2a and Figures S5-14). The X-ray structure of **1** revealed that one CO ligand is eclipsed with the carbonyl function of L. Hereafter, the α -isomer denotes the complex corresponding to the release of this specific CO ligand. The two remaining isomers, denoted β and γ , are anticipated to be very similar. Figure 2b-d gathered the results obtained for

the α - and β -isomers. Those for the γ -isomers, close to those of the β -isomer, are presented in Figure S14.

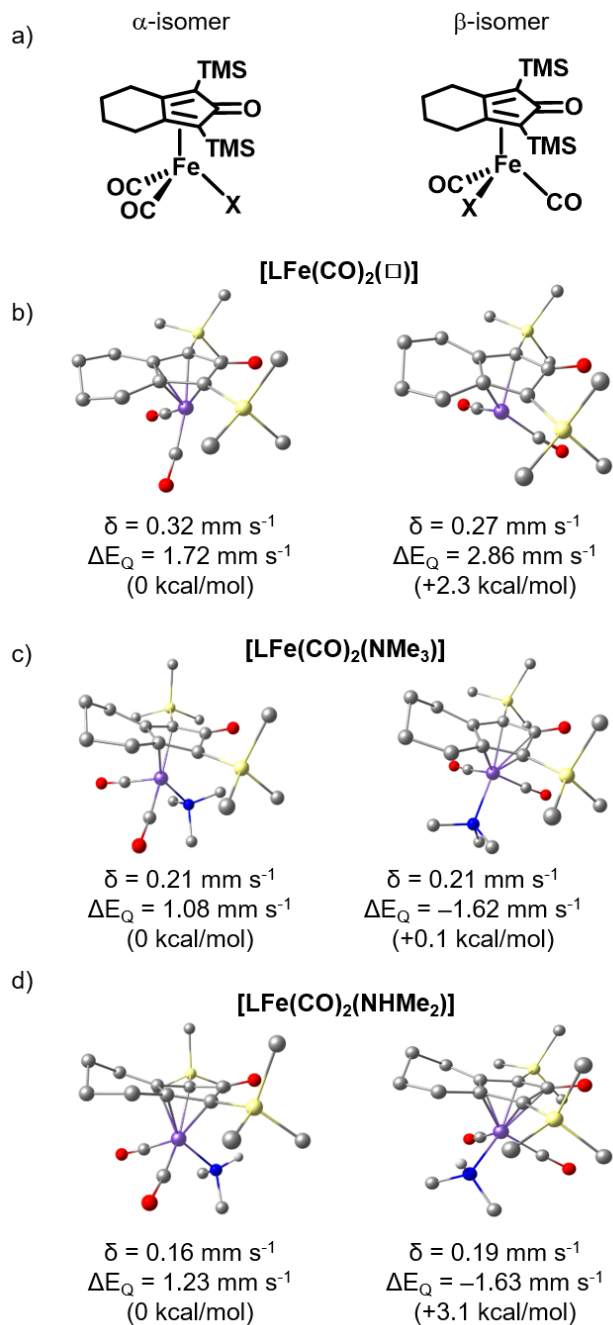


Figure 2. (a) Scheme of the α - and β -isomers of $[\text{LFe}(\text{CO})_2(\text{X})]$ ($\text{X}=\text{vacant}, \text{NMe}_3, \text{NHMe}_2$). (b-

d) Geometry optimized structures and corresponding calculated Mössbauer parameters δ and

ΔE_Q . H atoms omitted for clarity except for the secondary amine. Relative energies of the α - and β -isomers in each series of complexes are indicated in brackets.

Whatever the isomer, the removal of one CO, a strong π -acceptor ligand, leads to a significant increase of the isomer shift compared to that of the pre-catalyst ($\approx 0.3 \text{ mm s}^{-1}$ for $[\text{LFe}(\text{CO})_2]$ versus 0.06 mm s^{-1} for **1**). As expected, this increase is partially compensated by the coordination of an amine, NMe_3 or NHMe_2 ($\approx 0.2 \text{ mm s}^{-1}$). The isomer shift of $[\text{LFe}(\text{CO})_2(\text{NHMe}_2)]$ is low compared with that of $[\text{LFe}(\text{CO})_2(\text{NMe}_3)]$. This is surprising since the replacement of the trimethylamine by the weaker σ -donor NHMe_2 ligand should lead to a higher isomer shift. Deeper analysis of the bond lengths and Mayer bond orders shows that the Fe-N bond is more covalent in the case of $[\text{LFe}(\text{CO})_2(\text{NHMe}_2)]$ explaining the lower isomer shift (Figure S15). This is attributed to steric hindrance between the protons of NMe_3 and the cyclopentadienone ligand that precludes a short Fe-N bond.

Departure of one CO also leads to an increase of the quadrupole splitting (ΔE_Q , absolute values) that is reduced upon coordination of NMe_3 or NHMe_2 . In contrast to the isomer shifts, ΔE_Q values depend on the isomer. Lower values are determined for the α -isomers than for the β - and γ -forms. However, variations can't be simply related to the variations in the geometry around the iron.

A close examination of Figure 2 reveals that only the parameters of α - $[\text{LFe}(\text{CO})_2(\text{NMe}_3)]$ closely match those experimentally determined by Mössbauer. Accordingly, we propose species **3** to be the α - $[\text{LFe}(\text{CO})_2(\text{NMe}_3)]$ complex. Coordination of NMe_3 is supported by the characterization of related complexes. Several nitrile complexes $[\text{LFe}(\text{CO})_2(\text{NCR})]$ have been previously isolated and characterized upon reaction of 1.2–1.5 eq of Me_3NO on **1**.³⁶ Analogously, the complex $[\text{LFe}(\text{CO})_2(\text{HOCH}_2\text{Ph})]$ was characterized as resulting from the

reaction of **2** with benzaldehyde in toluene.³⁷ It is also remarkable to notice that the X-ray structures of $[\text{LFe}(\text{CO})_2(\text{HOCH}_2\text{Ph})]$ ³⁷ and of $[\text{L}'\text{Fe}(\text{CO})_2(\text{PPh}_3)]$ ($\text{L}' = 2,4$ -diphenylbicyclo[3.3.0]octa-1,4-dien-3-one)³⁸ have revealed a α -conformation, the O and P coordinated atoms being almost in the plane defined by the Fe ion and the L and L' ligand carbonyl function (O–C–Fe–(O/P) torsion angle lower than 3°). A symmetric structure has also been proposed for $[\text{LFe}(\text{CO})_2(\text{NMe}_3)]$ from its $^1\text{H-NMR}$ spectrum.³⁷ This is in line with calculated energy for the different isomers, evidencing the preferred α -conformation within the series of considered complexes (Figure 2). All together, these observations strongly sustain the generation of α - $[\text{LFe}(\text{CO})_2(\text{NMe}_3)]$ as the major species upon reaction of Me_3NO with **1**.

Next, we attempted to identify the structures compatible with the Mössbauer parameters determined for species **4** ($\delta = 0.51 \text{ mm s}^{-1}$ and $\Delta E_Q = 1.06 \text{ mm s}^{-1}$), keeping in mind that the large linewidth suggests a distribution of the nuclear parameters and thus a distribution for the Fe environment. It may already be noticed that the Mössbauer parameters calculated for $[\text{LFe}(\text{CO})_2]$, whatever the isomer, are well separated from the desired values, excluding the formation of this complex. Because the reaction of 1 equiv of trimethylamine-*N*-oxide on **1** is not complete, we hypothesized that unreacted Me_3NO may act on the generated complex **3**. Accordingly, we investigated the six different isomers of $[\text{LFe}(\text{CO})(\text{NMe}_3)]$ and the three of $[\text{LFe}(\text{CO})(\text{NMe}_3)_2]$, the latter resulting from the coordination of an additional trimethylamine in place of the released CO. The departure of two CO ligands from **1** leading to the formation of $[\text{LFe}(\text{CO})]$ was also considered. Details are presented in the Supporting Information and are summarized below. As it may be anticipated, Mössbauer parameters for $[\text{LFe}(\text{CO})]$ are larger than those of $[\text{LFe}(\text{CO})_2]$ ($\delta > 0.57 \text{ mm s}^{-1}$ and $|\Delta E_Q| > 2.9 \text{ mm s}^{-1}$, see Figure S16). These obtained values are indeed too high to support the formation of $[\text{LFe}(\text{CO})]$. Similarly, the

departure of one CO from $[\text{LFe}(\text{CO})_2(\text{NMe}_3)]$ induced increased isomer shifts for $[\text{LFe}(\text{CO})(\text{NMe}_3)]$ (δ ranging from 0.40 to 0.43 mm s^{-1} , see Figure S17), but significantly lower than that determined. Because the corresponding quadrupole splittings are also too large ($|\Delta E_Q|$ ranging from 2.16 to 2.57 mm s^{-1}), formation of $[\text{LFe}(\text{CO})(\text{NMe}_3)]$ was ruled out. Mössbauer parameters values calculated for $[\text{LFe}(\text{CO})(\text{NMe}_3)_2]$ are given in Figure 3. Based on the calculated energies, the α -isomer, corresponding to an eclipsed CO ligand with respect to the carbonyl group of L, is disfavored. ΔE_Q for the β - and γ -isomers are exceeding the desired value by $\approx 0.5 \text{ mm s}^{-1}$ whereas the isomer shifts are perfectly in agreement with the 0.5 mm s^{-1} observed value. It may be noted that former studies have evidenced the exchange of two carbonyl ligands in **1** by two acetonitrile molecules upon photochemical activation of **1** performed in CH_3CN , the resulting X-ray characterized $[\text{LFe}(\text{CO})(\text{NCMe})_2]$ complex presenting a β -conformation.³⁹ We are thus inclined to identify **4** as β - $[\text{LFe}(\text{CO})(\text{NMe}_3)_2]$.

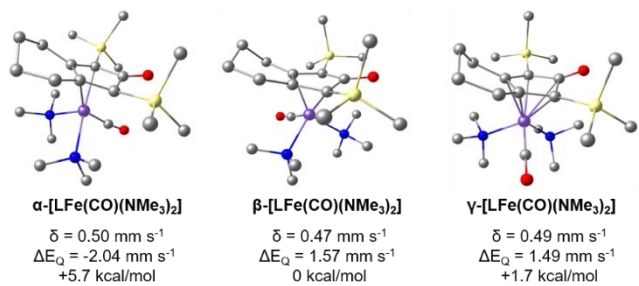


Figure 3. Geometry optimized structures of the three conformational isomers for $[\text{LFe}(\text{CO})(\text{NMe}_3)_2]$, computed Mössbauer nuclear parameters and relative energy (B3LYP).

¹³C NMR spectroscopy. In order to confirm the coordination of NMe_3 , we then performed an NMR study. The mixture obtained by reacting $[\text{LFe}(\text{CO})_3]$ with two equivalents of Me_3NO contains the species labeled **3** as major and was sufficiently stable on the NMR time scale to be

analyzed . With four equivalents of Me₃NO, the fast degradation of the mixture containing mostly the species labeled **4** precludes a similar study.

At magnetic fields above 9.4 T, corresponding to 400 MHz for ¹H NMR spectra, the dispersion is not high enough to distinguish in conventional one-dimensional spectra the protons of the precatalyst from the protons of the new species formed. ¹³C NMR shifts extend over a much larger range than proton shifts and are particularly suited to identify diamagnetic iron complexes, even in mixtures. We applied an inverse gated decoupled methodology in which proton decoupling is only applied during the acquisition period. In this case, no polarization transfer from ¹H to ¹³C via NOE takes place and therefore, the resulting ¹H-coupled ¹³C spectrum can be used for quantitative measurements.

Figure 4a shows the proton decoupled ¹³C NMR spectra of [LFe(CO)₃] taken in CDCl₃ solution at 298 K. Integral values for the different ¹³C resonances are identical to the expected values, demonstrating the efficiency of the methodology applied for quantitative measurements (Figure S20). To reduce the acquisition time without weakening the signal-to-noise ratio, a shorter relaxation time was applied (Figure 4a). A 3:6 quantitative ratio is still obtained for the resonance of the coordinated CO ligands and those from the methyl groups of the SiMe₃ substituents of L (Figure S21). The same methodology was then applied to measure the ¹³C NMR spectrum of the mixture obtained by reacting [LFe(CO)₃] with 2 equiv of Me₃NO (Figure 4b). All the characteristic resonances of [LFe(CO)₃] are observed but the spectrum is clearly dominated by the appearance of a new set of resonances attributed to the formation of a new species. This major species is characterized by the same number of resonances slightly shifted as compared to those of **1**. It is worth noticing the appearance of a new resonance at 58.2 ppm. The resonances at δ = 214.8 ppm and 0.82 ppm corresponding to the coordinated CO ligands and to

the SiMe₃ groups integrate for two and six, respectively, while the resonance at $\delta = 58.2$ ppm integrates for three (Figure S22). This is in agreement with the substitution of one CO by one trimethylamine ligand. The assignment of the resonance at $\delta = 58.2$ ppm to the methyl groups of Me₃N is corroborated by DEPT 135 measurement (Figure S23) and DFT calculations (Figure S19). A ratio of 7.3(\pm 0.5):1 for [LFe(CO)₂(NMe₃)]:[LFe(CO)₃] was determined based on the integrals of the CH₂ signals (see inset in Figure S22). These results are in line with the Mössbauer data showing that a few percent of unreacted precatalyst remain in solution (see Table 1).

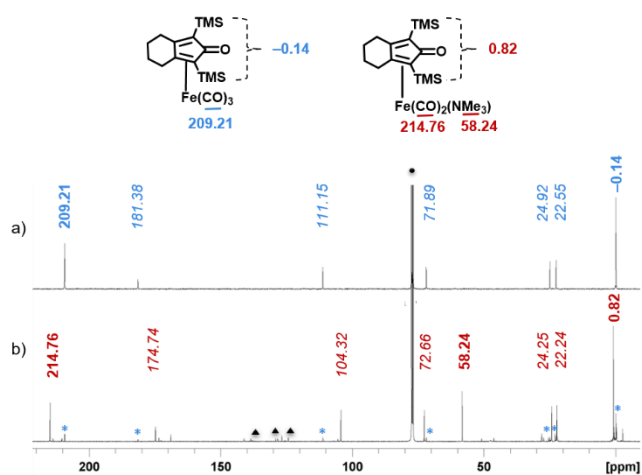


Figure 4. Inverse gated proton decoupled ¹³C NMR spectra recorded in CDCl₃ of complex [LFe(CO)₃] a) in absence of Me₃NO and b) reacted with 2 equiv of Me₃NO. T = 298 K. Blue stars denote [LFe(CO)₃] resonances, black triangles and dot denote toluene and chloroform solvent resonances, respectively.

DISCUSSION

Overall, these experimental and computational studies shed light on the type of species formed during chemical activation of (cyclopentadienone)iron carbonyl complexes and complement

previous studies carried out on photochemical activation. Indeed, it has been previously demonstrated that photocatalytic activation of $[\text{LFe}(\text{CO})_3]$ in acetonitrile at $-30\text{ }^\circ\text{C}$ gives rise to the formation of stepwise and reversible ligand exchange of all three carbonyl ligands by acetonitrile molecules.³⁹ In addition, studies conducted with (tetraphenylcyclopentadienone)iron carbonyl complex showed the reversible formation of the corresponding activated species with one vacant coordination site when the photocatalytic activation was performed in toluene in closed vial at room temperature.⁴⁰ Despite these studies underlying the role of the solvent and the reaction condition (open or closed vial) on the type of species formed by photochemical activation, too few studies take into account the type of species formed through chemical activation. The most employed methodology in the literature to activate the precatalyst relies on the use of trimethylamine-*N*-oxide as an external oxidant, generating CO_2 and NMe_3 as byproducts. $[\text{LFe}(\text{CO})_2]$ is often proposed as the activated complex resulting from this chemical activation, despite the coordinating capability of the generated trimethylamine (Figure 5).

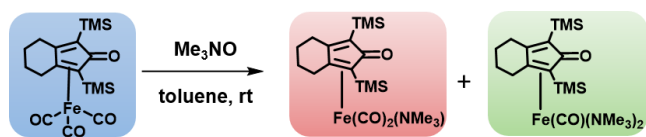


Figure 5. Revisited scenario for the chemical activation of (cyclopentadienone)iron carbonyl complex in absence of substrate.

Our studies evidence that the use of Me_3NO leads to complexes with no vacant position, the released CO being replaced by the generated NMe_3 . We have shown here that the conversion of $[\text{LFe}(\text{CO})_3]$ is never complete when using from one up to four equivalents of Me_3NO at room temperature in toluene. The produced mixtures always contain the precatalyst and two new species in which one or two CO ligands are replaced by trimethylamine were identified. Hence,

under catalytic conditions, we anticipate that the coordination of the alcohol is in competition with that of the generated NMe_3 . It has been previously evidenced that the X ligand in preformed $[\text{LFe}(\text{CO})_2(\text{X})]$ (X representing phosphine, nitrile or pyridine type ligand) can be substituted by an alcohol.³⁷ Thus, formation of $[\text{LFe}(\text{CO})_2(\text{NMe}_3)]$ may not be detrimental for the catalysis but may reduce the catalytic efficiency of the iron complex. Note that heating the solution at 35°C for 20 minutes did not lead to the formation of the 16-electron complex $[\text{LFe}(\text{CO})_2]$. Generation of NMe_3 , that is a base, may interfere with the acidic conditions used for the catalysis in some cases. Accordingly, this system cannot be considered as a base-free catalyst. This has been circumvented by the employment of preformed $[(\text{HL})\text{FeH}(\text{CO})_2]$ or $[\text{LFe}(\text{CO})_2(\text{NCR})]$ where only H_2 and RCN are liberated, respectively.^{41,42} Furthermore, we have shown here that Me_3NO also reacts with $[\text{LFe}(\text{CO})_2(\text{NMe}_3)]$. The coexistence of $[\text{LFe}(\text{CO})_2(\text{NMe}_3)]$ and $[\text{LFe}(\text{CO})(\text{NMe}_3)_2]$ irrespectively of the number of Me_3NO equivalents open the door to new questioning regarding the catalytic active species (Figure 5). As such, it demonstrates the crucial importance of the nature and the amount of pre-activating reagent over the reactivity.

CONCLUSION

A systematic study on reactions of $[\text{LFe}(\text{CO})_3]$ with different amounts of Me_3NO were performed to gain a deep understanding on the nature and on the distribution of the iron species formed. The combination of Mössbauer spectroscopy and DFT calculations allows us to evidence the formation of $[\text{LFe}(\text{CO})_2(\text{NMe}_3)]$ and $[\text{LFe}(\text{CO})(\text{NMe}_3)_2]$ upon reaction of Me_3NO on $[\text{LFe}(\text{CO})_3]$. No trace of the proposed active species, namely $[\text{LFe}(\text{CO})_2]$, was evidenced neither by Mössbauer spectroscopy nor by ^{13}C -NMR spectroscopy. When 2 equivalents of oxidant are used, $[\text{LFe}(\text{CO})_2(\text{NMe}_3)]$ is the major iron species formed. This complex may indeed be the key intermediate for the catalysis. We hope this work will provide useful and

valuable information to the scientific community using such type of catalyst to take into account the best activation pathway depending on the targeted transformation. These studies also shed light on the fact that the precatalyst and its corresponding active species exhibit significant differences in their electronic structures and are therefore distinguishable by Mössbauer spectroscopy. It opens the door to Mössbauer investigation of complex catalytic processes involving (cyclopentadienone)iron carbonyl complexes.

ASSOCIATED CONTENT

Supporting Information. The supporting information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem...>

Mössbauer spectra and analyses, UV/Vis studies, NMR measurements, computational studies and Cartesian coordinates of computed structures (PDF).

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest

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(cyclopentadienone)iron carbonyl complexes are versatile catalysts for hydrogenation or transfer hydrogenation reactions including the *N*-alkylation of amines with alcohols. In this study, we report on the species formed during the course of the pre-catalyst activation with the Me_3NO chemical reagent.

