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Ligand Adducts of Bis(acetylacetonato)iron(II): A ^{1}H NMR Study

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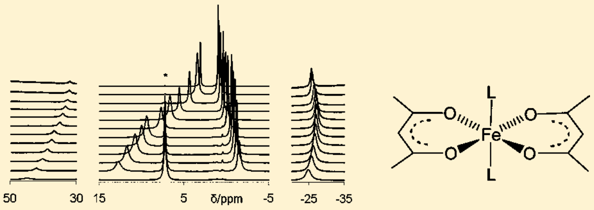
S *Supporting Information*

ABSTRACT: We report here a thorough ^{1}H NMR study of $Fe(acac)_2$ solutions in a wide variety of noncoordinating and coordinating solvents, as well as the interaction of this complex with Et_3N, pyridine, PMe_2Ph, and $R_2PCH_2CH_2PR_2$ [R = Ph (dppe), Et (depe)] in C_6D_6. The study reveals that $Fe(acac)_2$ is readily transformed into $Fe(acac)_3$ in solution under aerobic conditions and that the commercial compound is usually contaminated by significant amounts of $Fe(acac)_3$. The ^{1}H NMR resonances of $Fe(acac)_2$ are rather solvent-dependent and quite different than those reported in the literature. The compound is unstable in $CDCl_3$ and stable in CD_2Cl_2, C_6D_6, CD_3CN, acetone-d^6, DMSO-d^6, THF-d^8, and CD_3OD. The addition of the above-mentioned ligands (L) reveals only one paramagnetically shifted band for each type of acac and L proton, the position of which varies with the L/Fe ratio, consistent with rapid ligand exchange equilibria on the NMR time scale. A fit of the NMR data at a high L/Fe ratio allows the calculation of the expected resonances for all protons in the $Fe(acac)_2L_2$ molecules. The system with the bidentate depe ligand shows evidence for a slow ligand exchange at low depe/Fe ratios, proposed to involve a species with the *cis*-chelated mononuclear $Fe(acac)_2$(depe) structure, whereas the fast exchange at a higher ratio is proposed to involved a *trans*-$Fe(acac)_2(\kappa^1\text{-depe})_2$ complex. Complex $Fe(acac)_2$(dppe) cannot be investigated in solution because of low solubility in a noncoordinating solvent and because of the poor dppe competition for binding in coordinating solvents. The compound was crystallized, and its X-ray structure reveals a 1-dimensional polymeric structure with dppe-bridged Fe centers having the *trans*-octahedral $Fe(acac)_2(\kappa^1\text{-dppe})_2$ coordination environment.



■ INTRODUCTION

Nuclear magnetic resonance spectroscopy is one of the most useful characterization tools for molecular chemistry, mostly applied for the analysis of the proton distribution in molecular compounds in solution.[1,2] It is also a powerful tool for the study of dynamic phenomena occurring in solution when the rate of chemical exchange between nonequivalent sites falls in the same range as the chemical shift difference.[3] Most routine analyses are limited to diamagnetic compounds, because the strong dipolar coupling between the magnetic moments associated with the observed nuclear spin and the electronic spin in paramagnetic systems causes very rapid relaxation of the nuclear states and consequent broadening of the resonance signal, sometimes so severe that the peak disappears below the noise level. However, under suitable conditions (rapid relaxation of the electronic spin system, generally restricted to spin systems different from the doublet state, $S = 1/2$), the relaxation of the nuclear state is sufficiently slow to yield visible signals, albeit characterized by a large paramagnetic shift. Thus, informative spectra can be obtained when opening the data collection window to a much wider frequency range relative to diamagnetic compounds.[4] For instance, ^{1}H NMR resonances, usually restricted within the 0−15 ppm range for diamagnetic compounds, may be spread over several hundreds of parts per million for paramagnetic compounds. The ^{1}H NMR investigation of paramagnetic molecules in solution is now a very powerful tool,[5] especially for the investigation of the coordination sphere of paramagnetic metals and metal clusters in proteins.[6] NMR is also a preferred technique for the investigation of ligand exchange processes for paramagnetic complexes.[7,8] Yet, the technique is seldom employed for the investigation of the structure and speciation of simple paramagnetic coordination compounds.[9] Certain simple complexes that attracted considerable attention many decades ago in terms of their basic coordination chemistry have never been investigated by ^{1}H NMR, even though they exhibit sufficiently resolved resonances, or the investigation has not been carried out in sufficient detail. This is the case for $Fe(acac)_2$.

Compound $Fe(acac)_2$ has been known for a long time, the typical synthetic procedure being the reaction of aqueous $FeCl_2$ with acetylacetone in the presence of a base.[10] It is commercially available and inexpensive. The study of its structure in the solid state and in solutions of coordinating solvents as well as noncoordinating ones attracted considerable attention in the 1960s and 70s. The compound crystallizes in the form of a tetramer with two O-bridged dinuclear units that are further held together by a rather long Fe−C bond between the inner Fe atom of one unit with one acetylacetonate central

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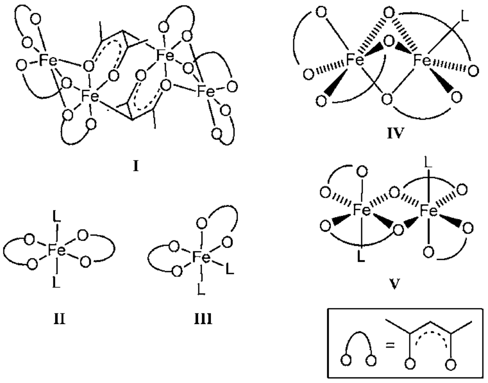
C atom of the adjacent one, as shown in Chart 1 (**I**).[11] In the presence of neutral donor molecules, which may also be weakly binding solvent molecules, mononuclear bis-ligand adducts are formed. The bis-aqua derivative with a *trans* geometry (**II**) has been crystallographically chartacterized,[12] and other derivatives with the same geometry have been reported for related bis(β-diketonato) compounds Fe(RCOCHCOR)$_2$ with R = CF$_3$ (L = THF,[13] *o*-diaminobenzene,[14] and the cyano function of the metalloligand CpFe(dppe)CN[15]), Ph (L = Et$_2$O),[16] and *t*Bu (L = 1,4-dioxane).[16] Derivatives with a *cis* geometry (**III**) have also been crystallographically characterized in the presence of chelating ligands, such as Fe(CF$_3$COCHCF$_3$)$_2$(L$_2$) with L$_2$ = Me$_2$NCH$_2$CH$_2$NMe$_2$[17] and 2-(2-pyridyl)-4,6-bis(trifluoromethyl)pyrimidine.[18]

Chart 1. Structures Observed for Fe(acac)$_2$ and Its Ligand Adducts



From the above data, it is clear that ligand binding to Fe(acac)$_2$ is not very strong, particularly with weak donors. When this compound is dissolved in a coordinating solvent, it is then possible to imagine that solvent-dependent equilibria between different species may be established. The solution behavior of Fe(acac)$_2$ has been studied by a variety of methods. Cryoscopic and ebullioscopic measurements indicate that the compound is monomeric in dilute benzene solutions, and a tetrahedral structure was deduced from powder X-ray photographs.[19] The titration of a dilute benzene solution with pyridine, monitored by UV−visible spectroscopy, was shown to lead successively to three different species, formulated as [Fe(acac)$_2$]$_2$py, [Fe(acac)$_2$py]$_2$, and Fe(acac)$_2$py$_2$.[20] Possible structures for the dinuclear species are **IV** and **V** (Chart 1), identical to those of cobalt and nickel analogues.[21] There is only one report of the ^{1}H NMR properties of Fe(acac)$_2$, in the absence of donor molecules (C$_6$D$_6$ solution), according to which the compound exhibits two resonances at δ 0.8 for the CH and 17.5 for the CH$_3$ protons.[22]

In this contribution, we report a more detailed ^{1}H NMR study of Fe(acac)$_2$ in the presence of a variety of donor ligands including phosphines and the X-ray structure of the adduct with the bidentate diphosphine ligand bis(diphenylphosphino)ethane (dppe). The results highlight the power of ^{1}H NMR for assessing the behavior of Fe(acac)$_2$ in solution and the relative binding strength of different ligands. The study has also unexpectedly revealed that commercially available Fe(acac)$_2$ is generally contaminated by a significant amount of Fe(acac)$_3$.

■ EXPERIMENTAL SECTION

General. All solvents used in the reactions were distilled under argon. The NMR solvents were purchased from Euriso-top as single vials packaged under argon and used as received. The NMR spectra were recorded on Bruker ARX250 or DPX300 instruments. Chemical shifts are expressed in parts per million downfield from Me$_4$Si. All spectra were recorded at a temperature of 298 K, which was maintained in the NMR probe by an automatic regulation device and was regularly checked by the 4% methanol and 80% glycol ^{1}H NMR methods; the observed maximum temperature fluctuation in the probe was ±2 K. The Fe(acac)$_2$ material used for this study was either purchased from Aldrich or synthesized from FeCl$_2$ according to the published procedure,[10] working under the most rigorous exclusion of air using Schlenk line techniques. The white anhydrous FeCl$_2$ precursor was prepared immediately prior to the synthetic procedure by refluxing anhydrous FeCl$_3$ and metallic Fe in dry THF.[23] All of the ^{1}H NMR investigations of the ligand addition equilibria were carried out using the commercial Fe(acac)$_2$, since the Fe(acac)$_3$ impurity present in this sample (see Results and Discussion) was found to be completely inert toward the addition of any of the ligands used. The Fe(acac)$_2$ concentration was calculated taking into account the amount of Fe(acac)$_3$ impurity (estimated from the integration of the CH$_3$ resonances of the two compounds).

Synthesis of Fe(acac)$_2$(dppe). Fe(acac)$_2$ (200 mg, 0.787 mmol) and dppe (376 mg, 0.944 mmol) were dissolved in 20 mL of CH$_2$Cl$_2$. Stirring at room temperature produced a golden yellow precipitate within a few minutes. After 2 h, the solid was collected by filtration and dried (260 mg, 50.6%). The solid was dissolved in 10 mL of THF and the resulting solution layered with 50 mL of pentane. Black crystals (150 mg) were obtained via diffusion overnight.

X-Ray Crystallography. A single crystal was mounted under inert perfluoropolyether on the tip of a cryoloop and cooled in the cryostream of an Oxford-Diffraction XCALIBUR SAPPHIRE-I CCD diffractometer. Data were collected using monochromatic Mo Kα radiation (λ = 0.71073). The structure was solved by direct methods (SIR97)[24] and refined by least-squares procedures on F^2 using SHELXL-97.[25] All H atoms attached to carbon were introduced in idealized positions and treated as riding on their parent atoms in the calculations. The drawing of the molecule was realized with the help of ORTEP3.[26,27] Crystal data and refinement parameters are shown in Table 1.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 833545. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223−336−033; e-mail: deposit@ccdc.cam.ac.uk).

■ RESULTS

a. Solution Properties of Fe(acac)$_2$ in Various Solvents.

^{1}H NMR spectra of a commercially available sample of Fe(acac)$_2$ in a variety of different solvents are shown in Figure 1. With the exception of CDCl$_3$ (to be discussed further down), three broad resonances are observable, a first one (strongly solvent dependent) in the δ 50−25 range, a second one (solvent independent) at δ 21, and a third one (slightly solvent dependent) at δ −25 to −31. The possibility that these resonances result from the nonequivalence of protons in a structure as observed in the solid state (**I** in Chart 1) is discarded by the observed behavior in the presence of donor molecules, known to form symmetric mononuclear adducts. In this context, the solvent independent resonance at δ 21 is puzzling. Note that the latter resonance becomes the major one observed in CDCl$_3$, accompanied by another strong and broad resonance at δ 2.0 which is absent in the other solvents, and by a much weaker and broad resonance at ca. δ −29, whereas the

Table 1. Crystal Data and Structure Refinement for $Fe(acac)_2(dppe)$

empirical formula	$C_{36}H_{38}FeO_4P_2$
fw	652.45
temp	180(2) K
wavelength	0.71073 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimensions	a = 8.7676(4) Å
	b = 9.9352(5) Å
	c = 10.4923(5) Å
	α = 76.145(4)°
	β = 88.541(4)°
	γ = 66.314(5)°
volume	810.04(7) $Å^3$
Z	1
density (calcd)	1.337 Mg/m^3
abs coeff	0.602 mm^{-1}
F(000)	342
cryst size	0.55 × 0.17 × 0.13 mm^3
θ range for data collection	2.65−26.37°.
index ranges	$-10 \le h \le 10$, $-12 \le k \le 12$, $-12 \le l \le 13$
reflns collected	7287
independent reflns	3305 [R(int) = 0.0238]
completeness to θ = 26.37°	99.8%
absorption correction	Semiempirical from equivalents
max. and min transmission	1.00000 and 0.82268
refinement method	Full-matrix least-squares on F^2
data/restraints/params	3305/0/198
goodness-of-fit on F^2	1.044
final R indices [$I > 2\sigma(I)$]	R1 = 0.0277, wR2 = 0.0737
R indices (all data)	R1 = 0.0344, wR2 = 0.0771
largest diff. peak and hole	0.455 and −0.293 e $Å^{-3}$

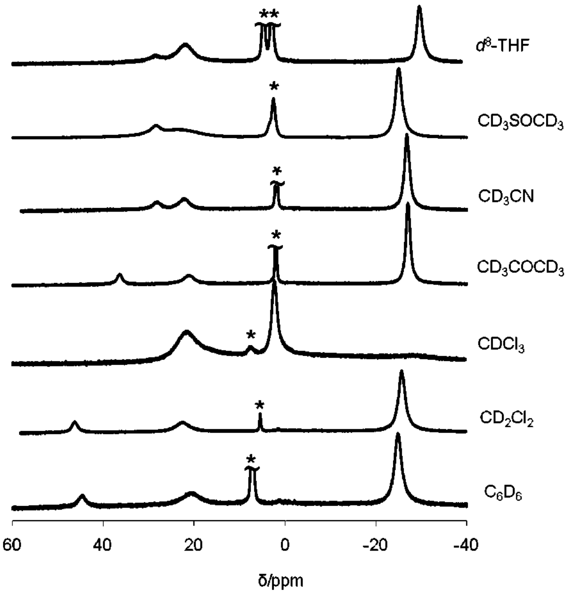


Figure 1. ^1H NMR spectra of commercial $Fe(acac)_2$ in a variety of solvents. The starred resonances belong to the solvent.

resonances in the δ 50−25 (weak) and −25 to −31 (strong) ranges seen in the other solvents are absent in $CDCl_3$.

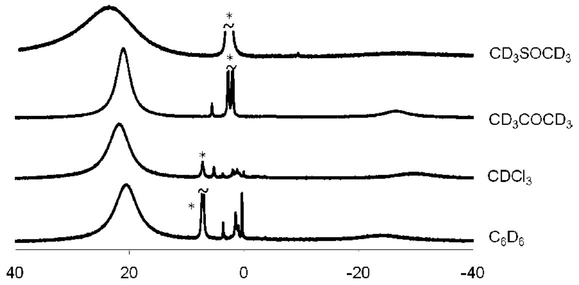


Figure 2. ^1H NMR spectra of $Fe(acac)_3$ in a variety of solvents. The starred resonances belong to the solvent, and the other sharp resonances in the δ 0−5 range are attributed to minor diamagnetic impurities.

The solution to this puzzle was provided by measurement of the ^1H NMR spectra of $Fe(acac)_3$ in various representative solvents, shown in Figure 2. The compound is characterized by two broad bands, which are essentially solvent independent, in agreement with the coordinative saturation of the complex, at δ ca. 21 and −25. Their relative ratio agrees with their assignment to the CH_3 and CH protons, respectively. The bandwidth is somewhat solvent-dependent, being slightly sharper in acetone and broader in DMSO. The chemical shift and peak width are not significantly concentration dependent, as shown by a study in DMSO in the 0.04−0.2 M range of concentrations. This spectrum is consistent with that reported in the literature (δ 20.7 and −27.4 in $CDCl_3$)[22] and with the expected high symmetry of the complex (ideal D_3), yielding a single resonance for each type of proton. It is therefore quite clear that the commercial $Fe(acac)_2$ compound is contaminated by $Fe(acac)_3$. Subtraction of the $Fe(acac)_3$ resonances from the spectra of commercial $Fe(acac)_2$ yields two bands for $Fe(acac)_2$: a low intensity one, assigned to the methyne protons and quite solvent dependent, in the δ 50−25 range and a high intensity one, assigned to the methyl protons and less solvent dependent, in the −25 to −31 range. Note that the weaker upfield resonance of $Fe(acac)_3$ overlaps with the stronger $Fe(acac)_2$ resonance and is hence not visible in the spectra of Figure 1.

Our own synthetic efforts following the original procedure[10] confirmed the facile contamination of $Fe(acac)_2$ by $Fe(acac)_3$, yielding a sample very much like that obtained from commercial sources. A major obstacle is the use of $FeCl_2$ that may be contaminated by Fe^{III} impurities. The use of a modified synthetic procedure[19] that makes use of sodium dithionite to reduce the Fe^{3+} impurities to Fe^{2+} indeed yielded a drastic reduction of the $Fe(acac)_3$ content, but a minor band at δ ca. 21 due to this impurity persisted. The cleanest $Fe(acac)_2$ sample, in our hands, was obtained by the standard procedure[10] when carried out under the most rigorous exclusion of air and from an anhydrous $FeCl_2$ sample generated *in situ* from anhydrous $FeCl_3$ and metallic Fe in boiling dry THF, a procedure also used by Wilkinson for an improved synthesis of ferrocene.[23] We have not found suitable conditions for efficient removal of the $Fe(acac)_3$ impurity from $Fe(acac)_2$ by recrystallization. The material obtained using this procedure shows the spectrum illustrated in Figure 3. Exposure of this solution to air results in the gradual replacement of these resonances with those of $Fe(acac)_3$ and in the deposition of a dark precipitate. No other resonances due to soluble compounds were observed in the spectrum. The ligand redistribution and precipitate observation make us propose the stoichiometry of eq 1, with the involvement of both oxygen and water from the moist air.

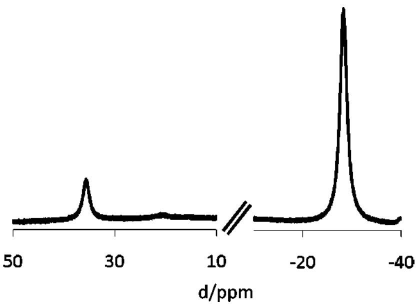


Figure 3. ^{1}H NMR spectrum of "clean" $Fe(acac)_2$ in C_6D_6. Note the small resonance at δ ca. 20, due to a very small residual amount of $Fe(acac)_3$.

$$6Fe(acac)_2 + 3/2O_2 + 3H_2O \rightarrow 4Fe(acac)_3 + 2Fe(OH)_3 \qquad (1)$$

In addition to a warning about the purity of commercially available $Fe(acac)_2$, the above observations lead to two conclusions. The first one is that, under any circumstance, all Me and CH protons are equivalent, which disagrees with the known solid state structure[11] but agrees with the solution molecular weight study that indicates a mononuclear formulation in dilute solution.[19] Clearly, if aggregation occurs in solution, it must be weak and must lead to rapid dynamic averaging of all chemically nonequivalent positions. The second conclusion is that our observed ^{1}H NMR spectrum for $Fe(acac)_2$ in C_6D_6 is dramatically different from that reported in the literature (see Introduction), whereas those of $Fe(acac)_3$ are in relatively good agreement (the spectra of the two compounds were reported in the same contribution).[22]

The behavior of $Fe(acac)_2$ in $CDCl_3$ deserved additional discussion. As seen in Figure 1, the resonances of $Fe(acac)_2$ are not present, whereas those of $Fe(acac)_3$, identical to those of the genuine sample (Figure 2), remain. On the other hand, a new relatively strong resonance is observed at ca. δ 1.9. This resonance is obtained reproducibly, but its line width appears quite concentration dependent (broader at lower concentrations). Hence, a chemical reaction completely consuming $Fe(acac)_2$ has occurred. One possibility that comes to mind is oxidation to $FeCl(acac)_2$, a known compound[28] (note that chloroform is a well-known Cl atom donor), according to eq 2. Dichloromethane is less prone to Cl atom transfer because of its stronger C−Cl bonds,[29] and indeed $Fe(acac)_2$ is stable in this solvent. The ^{1}H NMR spectrum for compound $FeCl(acac)_2$ has apparently not been reported; therefore, we have prepared it by one of the reported methods,[30] which consists of the comproportionation of $Fe(acac)_3$ and anhydrous $FeCl_3$ in a 2:1 ratio. However, the ^{1}H NMR spectrum of this compound in $CDCl_3$ shows a strong and broad resonance at δ 16.4, rather than at δ ca. 1.9, and a smaller broad resonance at δ −38.9. These resonance are rather close to those of $Fe(acac)_3$, and it is thus possible that $FeCl(acac)_2$ is present, together with the $Fe(acac)_3$ impurity, in the spectrum shown in Figure 1. However, this compound does not account for the observed band at δ 1.9. We have also considered the possibility that $FeCl(acac)_2$, once formed, further reacts with $Fe(acac)_2$ to yield a mixed-valence adduct (eq 3). However, an independent test shows that the two compounds do not react with each other in dichloromethane. Therefore, the nature of this product remains for the moment undetermined, but it is most definitely resulting from a reaction between $Fe(acac)_2$ and chloroform.

$$Fe(acac)_2 + CHCl_3 \rightarrow FeCl(acac)_2 + CHCl_2^{\bullet} \qquad (2)$$

$$FeCl(acac)_2 + Fe(acac)_2 \nrightarrow Fe_2Cl(acac)_4 \qquad (3)$$

b. Addition of Neutral Ligands to $Fe(acac)_2$. The coordination chemistry of $Fe(acac)_2$ with respect to a few neutral ligands (Et_3N; pyridine; and the phosphine ligands $PhPMe_2$, $Ph_2PCH_2CH_2PPh_2$, and $Et_2PCH_2CH_2PEt_2$) was investigated by means of the ^{1}H NMR technique. We start our analysis with the study of the NEt_3 addition to $Fe(acac)_2$ in C_6D_6, shown in Figure 4. Binding of NEt_3 to the Fe center is indicated by the paramagnetic shift experienced by the triethylamine methylene and methyl resonances at low NEt_3/Fe ratios. The shift is of opposite sign for the methylene (positive spin density) and methyl (negative spin density) resonances. Even for the maximum ratio of 30:1 used in the study, the resonance of the NEt_3 protons has not yet reached the typical value of the free ligand in a diamagnetic environment (e.g., δ 3.09 instead of 2.40 for the methylene resonance),[31] while the broadening caused by the exchange with the paramagnetic center is still sufficient to hide the typical H−H coupling, see Figure 5. The observation of a single resonance for each type of acac proton and also for each type of NEt_3 proton signals the presence of chemical exchange between $Fe(acac)_2$ and all of its possible $Fe(acac)_2L_x$ adducts, on one side, and between the $Fe(acac)_2L_x$ adducts and free L, on the other side, at the fast exchange limit on the NMR time scale. The stronger paramagnetic shift for the CH_2 protons than for

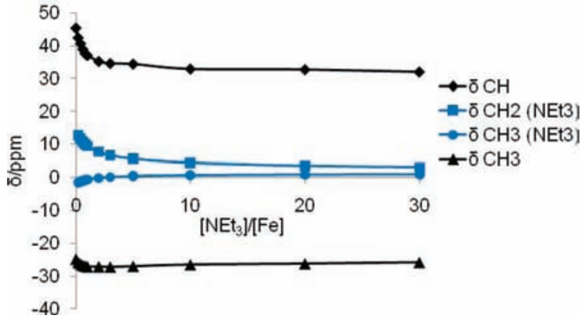


Figure 4. ^{1}H NMR chemical shifts observed for a solution of $Fe(acac)_2$ in C_6D_6 in the presence of variable amounts of NEt_3. $[Fe(acac)_2] = 8 \times 10^{-2}$ M.

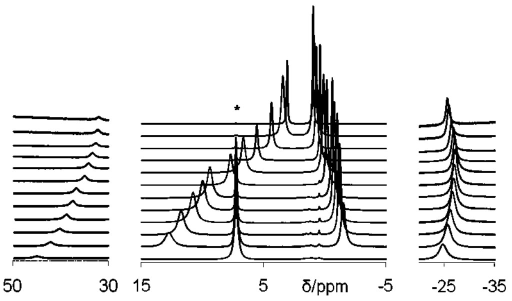


Figure 5. Excerpts in three different regions of the ^{1}H NMR spectra measured for a solution of $Fe(acac)_2$ in C_6D_6 in the presence of variable amounts of NEt_3. $[Fe(acac)_2] = 8 \times 10^{-2}$ M. The NEt_3/Fe ratios on going from bottom to top are 0, 0.2, 0.4, 0.6, 0.8, 1, 2, 3, 5, 10, 20, and 30. The starred resonance belongs to the solvent.

the CH_3 protons in NEt_3 is the result of closer proximity of the former to the paramagnetic center when the ligand is coordinated, with transmission of greater spin density. Concerning the resonances of the acac ligand, both continue to move up to the maximum NEt_3/Fe ratio used in the experiment. Both shift initially upfield with the acac CH_3 resonance being less affected than the CH resonance. The former moves slightly back downfield for NEt_3/Fe ratios greater than 3, probably because of a solvent effect on the $Fe(acac)_2(NEt_3)_2$ resonance and not because of changes in the equilibrium between the different $Fe(acac)_2(NEt_3)_x$ species.

Pyridine also binds the compound reversibly with rapid ligand exchange processes. As shown in Figure 6, the pyridine resonances are very much shifted from their normal position, all in the downfield direction (positive spin density on all aromatic protons). The assignment is based on the relative intensity (2:2:1 for *o*, *m*, and *p*), the broader and more paramagnetically shifted resonance being attributed to the *ortho* protons on the reasonable grounds that its greater proximity to the paramagnetic center allows the transmission of a higher spin density. The same hypothesis was previously made for the related $Co(acac)_2(py)_x$ adducts[32] and agrees with the assignments made on the basis of the comparison with picoline derivatives.[33] The resonances of the acac protons experience a more dramatic change relative to the previously discussed addition of NEt_3. Unfortunately, the methyne resonance is no longer discernible beyond a py/Fe ratio of 5 because of its large bandwidth, a small relative intensity, and its overlap with the stronger pyridine bands. The more clearly visible acac CH_3 resonance exhibits (like the methyne resonance) a significant upfield shift, up to a py/Fe ratio of 3 and then essentially no more change. This is an indicator of the stronger binding ability of pyridine relative to NEt_3, a result that parallels that of the related study with $Co(acac)_2$.[32]

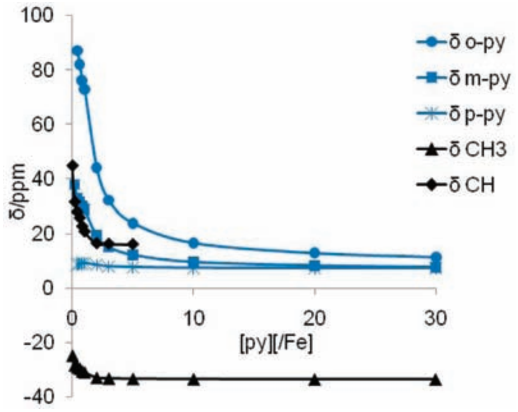


Figure 6. ^1H NMR chemical shifts observed for a solution of $Fe(acac)_2$ in C_6D_6 in the presence of variable amounts of pyridine. $[Fe(acac)_2] = 8 \times 10^{-2}$ M.

The chemical shift variations induced by the addition of PMe_2Ph are summarized in Figure 7. The behavior of this ligand grossly parallels that observed for NEt_3 and pyridine: only a single resonance for each type of proton in the acac and PMe_2Ph ligands, showing fast exchange. Note that the resonances of the acac ligand still shift as a function of the PMe_2Ph/Fe ratio for ratios greater than 10, similar to the behavior observed during the addition of NEt_3 and different from that observed during the addition of pyridine. This is a signal of the stronger binding ability of pyridine relative to the other ligands (see Discussion). Concerning the PMe_2Ph signals, the Me protons experience a very large downfield shift, much greater than for the methylene protons of the NEt_3 ligand that are separated from the Fe center by the same number of bonds, indicating more efficient transmission of spin density through the P donor. The aryl protons also experience a significant paramagnetic shift, downfield for *meta* and upfield for *ortho* and *para*. The chemical shift pattern of the PMe_2Ph protons in this compound is very similar to that observed in the tetrahedral compound $Fe(Se\text{-}2,6\text{-}C_6H_3iPr_2)_2(PMe_2Ph)_2$,[34] especially at low P/Fe ratio for what concerns the absolute values of the isotropic shifts.

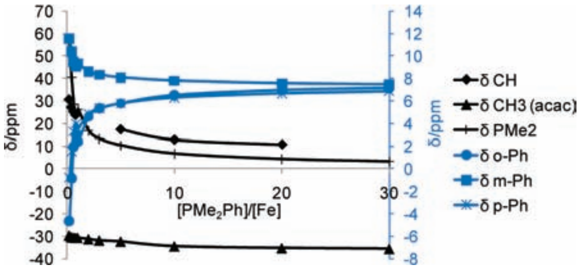


Figure 7. ^1H NMR chemical shifts observed for a solution of $Fe(acac)_2$ in C_6D_6 in the presence of variable amounts of PMe_2Ph. $[Fe(acac)_2] = 8 \times 10^{-2}$ M.

The observation of relatively weak binding of $Fe(acac)_2$ by a relatively strong field ligand such as PMe_2Ph encouraged us to explore the coordination behavior of a phosphine ligand with a greater electron donating power and a bidentate chelating coordination mode, namely, $Et_2PCH_2CH_2PEt_2$ (depe), hoping to obtain a less labile adduct. Contrary to the complexes containing monodentate ligands, which presumably preferentially generate symmetrical *trans* adducts, a mononuclear adduct with a short bite chelating ligand such as depe must necessarily adopt a *cis* configuration. In spite of the stronger anticipated binding properties, however, this ligand also leads to dynamic properties similar to those of the above examined monodentate ligands, as shown in Figure 8. Note in particular the continuous shift of the acac resonances up to depe/Fe ratios greater than 10. The paramagnetic shifts experienced by the phosphine α-H nuclei are quite similar to that experienced by the Me protons in the PMe_2Ph adduct (cf. with Figure 7), whereas the β-H nuclei are much less shifted. As pointed out above for the PMe_2Ph adduct, the pattern of chemical shifts for the $Et_2PCH_2CH_2PEt_2$ ligand in the $Fe(acac)_2$ adduct is also very similar to that reported for the tetrahedral complex Fe(Se-2,6-

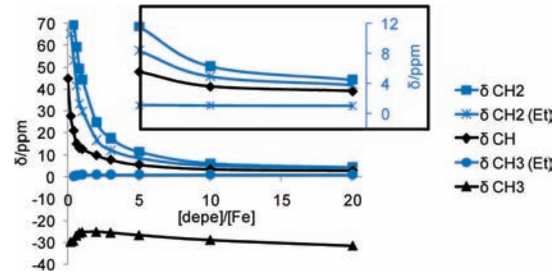


Figure 8. ^1H NMR chemical shifts observed for a solution of $Fe(acac)_2$ in C_6D_6 in the presence of variable amounts of $Et_2PCH_2CH_2PEt_2$. $[Fe(acac)_2] = 8 \times 10^{-2}$ M.

$C_6H_3iPr_2)_2(Et_2PCH_2CH_2PEt_2)$.[34] A specific point of interest is the observation of a single resonance for the methylene protons of the Et substituent, whereas two are observed for complex $Fe(Se\text{-}2,6\text{-}C_6H_3iPr_2)_2(Et_2PCH_2CH_2PEt_2)$, as expected because these methylene protons become inequivalent (diastereotopic) upon coordination. This is in perfect agreement with the observed fast exchange between free and coordinated $Et_2PCH_2CH_2PEt_2$ in the $Fe(acac)_2$ complex, whereas a rigid structure is obtained for the tetrahedral bis(selenolate) compound.

A curious phenomenon is observed for these spectra at low depe/Fe ratios in the region of the depe Me protons (near 0 ppm), see Figure 9. If the complex were fully dynamic, only one resonance should be observed for each type of proton. However, the Me region of the depe ligand is characterized by several resonances, the most upfield shifted of which changes position, moving downfield, and increases in intensity as the depe/Fe ratio is increased, whereas the chemical shift and relative intensity of the other ones appear to be less sensitive to the depe/Fe ratio. For greater than 1 equiv of depe per Fe, only one resonance remains discernible. We tentatively interpret this phenomenon as indicating a slower chemical exchange between free phosphine (responsible for the resonances at δ 3−1) and a *cis*-coordinated chelating phosphine. This slower exchange would be a consequence of the chelate effect on the rate of chemical exchange. On the other hand, when the depe/Fe ratio increases, additional phosphine may coordinate and drive the system to the more favorable *trans* coordination, leading to fast exchange. This state of affairs is summarized in Scheme 1 (the five-coordinate intermediate may also adopt a dinuclear acac-bridged structure, as shown in Chart 1). Note that, contrary to the methyl protons, the methylene protons of the depe ethyl groups and backbone in the far downfield region show evidence for only one resonance for each different set. This may result from the much larger broadening of these resonances, not allowing the detection of any fine structure for the chemically inequivalent protons in the *cis*-chelated structure.

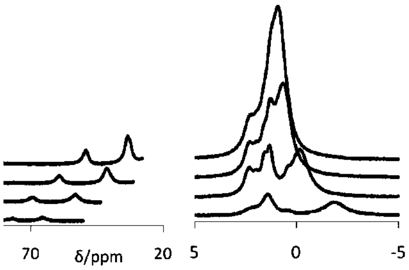
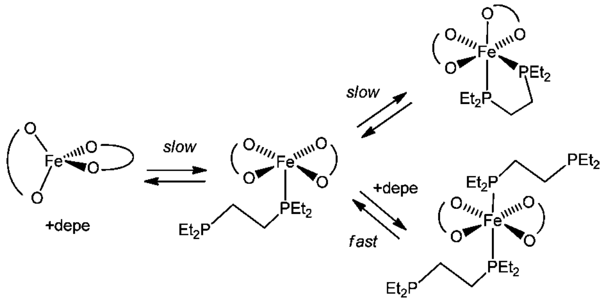


Figure 9. Representative regions of the ^1H NMR spectra of $Fe(acac)_2$ + depe in C_6D_6. $[Fe(acac)_2] = 8 \times 10^{-2}$ M and depe/Fe = 0.2, 0.4, 0.6, and 0.8.

Scheme 1. Proposed Structural Changes As the Consequence of depe Coordination to $Fe(acac)_2$



The above proposition cannot be proven in the absence of isolated samples of the 1:1 and 1:2 adducts. However, supporting evidence comes from the result of a reaction with the structurally related bis(diphenylphoshino)ethane ligand, dppe. An attempt to carry out a ^1H NMR monitoring of this reaction, by analogy with those described above, was hampered by the negligible solubility of the reaction product in C_6D_6 and in CD_2Cl_2. An analogous study could be carried out in d^8-THF, but this did not reveal any interaction between dppe and the Fe complex (the signals of dppe were observed at their regular diamagnetic position), probably because the THF solvent has a stronger binding capacity than dppe. The $Fe(acac)_2(dppe)$ adduct could be crystallized from a THF solution by diffusion of pentane, affording suitable single crystals for an X-ray analysis. Note that this compound had previously been reported and proposed to adopt a mononuclear *cis*-chelated structure.[35] On the other hand, our crystallographic study reveals a one-dimensional polymer, see Figure 10.

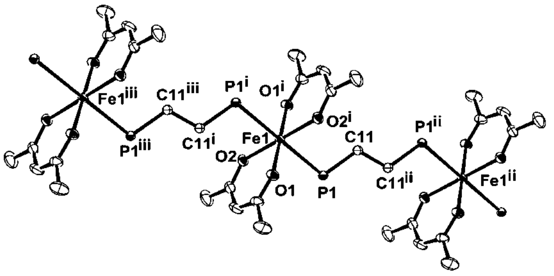


Figure 10. An ORTEP view of a fragment of the one-dimensional infinite chain observed for compound $Fe(acac)_2(dppe)$. The thermal ellipsoids are shown at the 50% probability level, and the H atoms as well as the phenyl rings have been removed for clarity. Relevant distances (Å) and angles (deg): Fe−P, 2.6496(4); Fe−O1, 2.0439(10) ; Fe−O2, 2.0617(10); P−Fe−O1, 90.72(3); P−Fe−O2, 92.19(3); P−Fe−O1^i, 89.28(3); P−Fe−O2^i, 87.81(3); O1−Fe−O2, 86.49(4); O1−Fe−O2^i, 93.51(4). Symmetry transformations used to generate equivalent atoms: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x, -y + 1, -z + 1$; (iii) $1 + x, y, z$.

The coordination geometry of each Fe center is *trans*-octahedral, as typically found in bis-adducts of bis(β-diketonato)iron(II) compounds.[12−16] This structure is the first one for this family of bis-adducts with a P-atom donor ligand. The Fe atom and the center of the C−C bond in the PCH_2CH_2P moiety sit on inversion centers. Consequently, all *trans* X−Fe−X angles are 180°. The symmetry-equivalent Fe−P distances of 2.6496(4) Å are rather long. The only other crystallographically characterized Fe^{II} complex with a P_2O_4 coordination sphere appears to be $Fe[P(CH_2CH_2O\text{-}Et)_2(CH_2Ph)]_2(O_3SCF_3)_2$, with Fe−P distances of 2.583(2) Å.[36] The FeX_2P_4 coordination geometry (X = halogen atom) is more represented, with 35 hits in the Cambridge crystallographic database. These structures are nicely divided into two sets as a function of the spin state, with 27 low spin (diamagnetic) compounds clustering around an average Fe−P distance of 2.26 Å with a standard deviation of 0.04 Å, while eight high spin (S = 2) compounds yield an average Fe−P distance of 2.62(5) Å. Most interesting are the two spin-crossover complexes $FeX_2(Ph_2PCH{=}CHPPh_2)_2$ (X = Cl, Br), for which the structure was recorded both above and below the transition temperature, yielding Fe−P distances of 2.312(8) and 2.289(9) Å for the low spin structure at 130 K, 2.592(2) and 2.576(2) Å for the high spin one at 295 K (X = Cl),[37] 2.326(4) and 2.294(4) Å for the low spin structure at 149 K, and 2.586(3) and 2.575(3) Å for the high spin one at 193 K (X = Br).[38] Thus, the Fe−P distance in an octahedral Fe^{II} complex may be taken as a direct gauge of the spin state, and the long distance observed for $Fe(acac)_2(dppe)$ is in good agreement with its paramagnetism. It is interesting to note that complex $FeCl_2(depe)_2$ was shown to have short Fe−P distances consistent with diamagnetism in the solid state, although a small population of the high-spin state occurs in solution.[39] Compound $Fe(acac)_2(depe)$ investigated in the present contribution, on the other hand, is clearly paramagnetic.

■ DISCUSSION

The NMR data collected during the present study clearly indicate that, for all tested neutral ligands, except perhaps for depe at a low ligand/Fe ratio, there is a very rapid exchange averaging each type of proton in the acac ligand (between all $Fe(acac)_2L_x$ complexes) and in the neutral ligand (between all $Fe(acac)_2L_x$ complexes and residual free L). Given our knowledge of the total metal and ligand concentrations and a model for the number and stoichiometry of the complexes present in solution, the data are amenable to a partial quantitative analysis. The major problem is the ratio between the number of parameters to be optimized (equilibrium constants and chemical shifts for each species) and the amount of available data (observed chemical shifts). The observed chemical shifts $\delta_{H,obs}$ for each different type of proton are averages of the chemical shifts of the same proton in each species, $\delta_{H,i}$, weighted by the population x_i of the species (eq 4, where the sum is extended over all species containing the observed proton). For a mixture of all species **I**−**V** shown in Chart 1 plus the free ligand (five species for each type of proton and four independent equilibria), nine independent parameters are needed. We may perhaps exclude species **III** from consideration, given that the *trans* isomer **II** is shown to be preferred, except for the chelating ligands at small L/Fe ratios (see Results). This reduces the number of independent parameters to seven for each type of proton. Even though the equilibrium constants are common for all different types of protons within the same ligand system, a global solution cannot be obtained with the small amount of available data points.

$$\delta_{H,obs} = \sum_i (x_i \delta_{H,i}) \tag{4}$$

A relatively simple analysis is possible, limited to the L resonances in the presence of a large ligand excess. Under these conditions, the bis-adduct should be by far the dominant species among all Fe complexes, hence to a first approximation $[Fe(acac)_2L_2] \sim$ total Fe concentration. This reduces eq 4 to eq 5, where there are no equilibrium constants and only two adjustable chemical shift parameters for the $[Fe(acac)_2L_2]$ complex and the free ligand L. The molar fractions x_{compl} and x_L are related to the ligand distribution and are known from the L/Fe ratio.

$$\delta_{H,obs}(\text{ligand protons}) = x_{compl}\delta_{H,compl} + x_L\delta_{H,L} \tag{5}$$

Restricting ourselves to the data points obtained with [L]/[Fe] ≥ 5 (or ≥2 for the more strongly binding pyridine), this analysis gives excellent fits and values of $\delta_{H,L}$ in excellent agreement with the known spectra of the free ligands. The $\delta_{H,compl}$ values for the $Fe(acac)_2L_2$ complexes resulting from these analyses are reported in Table 2. Plots showing the data fits and the extrapolated $\delta_{H,L}$ values are available in the Supporting Information. The table also reports the values of the acetylacetonate ligands in the same $Fe(acac)_2L_2$ complexes, from extrapolations of the observed $\delta_{H,obs}$ to infinite L/Fe ratios, as well as the reference resonances of ligand-free $Fe(acac)_2$.

Table 2. Calculated Chemical Shifts (δ) for Complexes $Fe(acac)_2L_2$ in C_6D_6 Solution at 298 ± 2 K

	L				
proton type	–	NEt_3	Py	PMe_2Ph	depe
o-CH			44.4	3.40	
m-CH			19.4	9.18	
p-CH			8.48	3.92	
PMe				22.7	
PCH_2CH_2P					25.4
CH_2(Et)		10.1			17.4
CH_3(Et)		−0.60			1.22
CH (acac)	44.6	31.7	15.7	8.3	2.0
CH_3 (acac)	−24.7	−25.8	−33.5	−36.3	−32.7

This type of analysis, leading to the extrapolation of paramagnetic shifts for rapidly exchanging ligands on paramagnetic complexes, does not appear to be frequently carried out, the majority of NMR studies for paramagnetic substances being limited to stable complexes with firmly bonded ligands.[9,40−49] For this reason, the values reported in Table 2 cannot be compared with literature precedents, because high-spin Fe(II) complexes that contain the same ligands have either not been investigated by ^1H NMR or their investigation does not consider the possible effect of reversible ligand dissociation/exchange on the NMR chemical shift. Interesting observations are the positive spin density transmitted to all aromatic protons of the coordinated pyridine, for which direct delocalization via ligand-to-metal and metal-to-ligand π interactions is possible, whereas alternating negative and positive spin density is found for the *o*-, *m*-, and *p*-aromatic protons of the PMe_2Ph ligand, for which the spin density is presumably transmitted mainly through a σ polarization scheme. The positive spin density on the aliphatic α-H atoms is greater and nearly equivalent in all P-atom donors (δ 22.7 in PMe_2Ph, 25.4 for the backbone, and 17.4 for the Et methylene protons in depe) than in NEt_3 (δ 10.1). The aliphatic β-H atoms in the Et substituents display a much smaller and negative shift, this time more important for the NEt_3 ligand. The effect of L bonding on the spin density transmitted to the acac ligands is also interesting. The effect is greater, as may be expected, on the CH resonance than on the CH_3 resonance, given that the former is directly linked to the pseudoaromatic six-membered cycle where π transmission of the spin density is possible. L binding greatly decreases the positive spin density on the CH proton, whereas it slightly increases the negative spin density on the CH_3 protons. The effect is less important for NEt_3, intermediate for pyridine, and greater for the phosphine ligands. This effect does not seem to correlate with the ligand binding strength, since pyridine appears to be the more strongly binding of the four ligands, as discussed above. However, the effect may correlate with the transmission of electron density from L to Fe.

Another interesting observation, revealed by comparing the data in Table 2 with the plots of each $\delta_{\mathrm{H,obs}}$ in the whole L/Fe range (Figures 3, 5, 6, and 7), concerns the need to invoke the presence of intermediate complexes $Fe(acac)_2L_x$ with $x < 2$. If the species present under all circumstances were just $Fe(acac)_2$ and $Fe(acac)_2L_2$, then the $\delta_{\mathrm{H,obs}}$ values for the ligand resonances could never experience a greater paramagnetic shift than those extrapolated for pure $Fe(acac)_2L_2$. However, this is essentially never the case. For instance, the PMe resonance in $Fe(acac)_2(PMe_2Ph)_2$ is calculated as δ 22.7, whereas this resonance is shifted up to δ 55.8 for a PMe_2Ph/Fe ratio of 0.2 (Figure 7). It can be concluded that a complex with a L/Fe ratio of 1 (like **V** in Chart 1) or 0.5 (like **IV** in Chart 1), or both, is characterized by greater paramagnetic shifts for each δ_H than **II**. This appears reasonable, since the spin density in **II** is transmitted from the metal to two L molecule and the overall effect on each should be smaller. As mentioned above, the number of data points for each resonance was too small for a more detailed analysis according to eq 4. However, this NMR titration method has the potential to provide fuller speciation information, if it is so desired, by carefully collecting a greater number of data points. We decided not to pursue such a detailed study but have outlined here the procedure allowing this to be done.

CONCLUSION

We have applied for the first time the powerful ^1H NMR spectroscopic analysis to the investigation of the coordination chemistry of a well-known compound, $Fe(acac)_2$. The study has not only corrected the erroneous assignment of the $Fe(acac)_2$ ^1H NMR resonances in an older report and highlighted the possible contamination of commercial $Fe(acac)_2$ by $Fe(acac)_3$ but also unveiled previously unappreciated features of the coordination chemistry of this compound with a variety of N-based and P-based ligands. The presence of rapid ligand exchange phenomena for paramagnetic substances is particularly amenable to investigation by the NMR technique, and a more general application of this approach merits consideration for the analysis of paramagnetic coordination compounds.

ASSOCIATED CONTENT

Supporting Information

Fitting of the chemical shift data for ligand resonances in the $Fe(acac)_2 + L$ systems (L = Et_3N, pyridine, PMe_2Ph, depe) at high L/Fe ratios (2 pages). Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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