A ^{13}C CP/MAS NMR Study of the Structure and Dynamics of [(η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$] Included in γ-Cyclodextrin: Evidence for Terminal−Bridging Exchange in the *cis* Isomer

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The novel inclusion compound of γ-cyclodextrin with the binuclear metal carbonyl complex (η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$ as guest molecule is reported. ^{13}C CP/MAS NMR spectroscopy, in the temperature range 100 to 353 K, is used to probe the structure and dynamics of the included molecules. Specifically, below ca. 240 K evidence is presented for the existence of both *cis* and *trans* isomers of included (η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$. Analysis of the temperature-dependence of the NMR line shapes shows that the microenvironment provided by the γ-cyclodextrin cavity allows much more extensive dynamic rearrangements of the guest molecules, in comparison to pure *cis*- or *trans*-(η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$, for which no isomerization or bridging−terminal carbonyl exchange processes are observed in this temperature regime. Notably, even at 100 K, bridging−terminal carbonyl exchange for the included *trans* isomer is rapid on the exchange-broadening time scale. However, the inclusion cavity is still more dynamically restrictive than a solution environment, and the rates of various exchange processes are usefully modified compared to those detected in solution. For (η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$ included in γ-cyclodextrin, contrary to the situation found in solution, the rate of bridging−terminal carbonyl exchange in the *cis* isomer is greater than the rate of *cis*−*trans* isomerization; in solution direct bridging−terminal exchange in the *cis* isomer could not be studied because indirect exchange via isomerization to the *trans* form, which undergoes rapid bridging−terminal exchange, is always significantly faster. By restricting isomerization, the inclusion environment thus confirms for the first time that the *cis* isomer is capable of carbonyl exchange and would allow the study of its rate and activation parameters.

Introduction

Cyclodextrins (CDs)[1,2] have been the subject of many articles and reviews, principally due to their versatility in including a wide variety of suitably sized guest molecules within their internal cavities.[3] The three commercially available cyclodextrin molecules (α, β, and γ) with their differing hydrophobic cavity sizes (diameters of 5.3, 6.5, and 8.3 Å, respectively) and aqueous solubilities have been used to facilitate the solubility in polar solvents of many organic and organometallic compounds of varying molecular size.

While the concept of including organometallic compounds in molecular cavities such as cyclodextrin macrocycles is not novel, the exploration of guest dynamics mediated by host−guest interactions has received more limited attention.[4] The modulation of the intermolecular host−guest interaction through motion will be dependent on the possible orientations of the guest within the cavity. Guest dynamics will occur only within the limitations of the intermolecular potentials determined by the size, shape, and dynamic flexibility of the guest molecule and the host cavity; thus delineation of the nature of any dynamic processes provides a means of studying aspects of the orientation of the organometallic guest within the cavity and the nature of the host−guest binding. This is particularly important for these cyclodextrin host−guest complexes with simple neutral organometallic guest molecules, which do not generally form as crystals suitable for single-crystal X-ray structure determination[5] and where, therefore, solid-state NMR methods remain a technique of choice for their structural elucidation.[6]

The earliest studies of solid-state dynamics involved the use of wide-line NMR methods to investigate the notable enhancement of reorientational motion of ferrocene and ruthenocene molecules[7−11] when included in cyclodextrin host cavities. More recently, studies on (arene)Cr(CO)$_3$[12] and simple binary metal

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carbonyl complexes such as $Fe(CO)_5$, $Mn_2(CO)_{10}$, and $Cr(CO)_6$ included in β- and γ-cyclodextrins[13] have highlighted the lowered activation energy barriers for specific molecular motions of the guest molecules, due to the structured nature of the cavity provided by the host molecule, which minimizes packing forces that would otherwise hinder the dynamic process. For $Fe(CO)_5$ and $Cr(CO)_6$ fast isotropic motion of the entire molecule occurs inside the CD cavity. The spectra of (arene)$Cr(CO)_3$ compounds are consistent only with rapid reorientation of both the C_6H_6 and the $(CO)_3$ unit about the principal molecular axis, suggesting guest molecule alignment with the cyclodextrin cavity axis. The hypothesis that the interplay of the symmetries, size, and resulting orientation of the guest molecule affects the nature of the intermolecular interactions between guest and host, and so ultimately determines the nature of the guest motion, is further considered and expanded in this article.

This present study reports variable-temperature (VT) ^{13}C CP/MAS NMR studies of the structure and dynamics of the novel inclusion compound of [(η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$] with γ-cyclodextrin. The study of [(η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$] has become a notable classic paradigm of fluxionality in carbonyl complexes containing metal−metal bonds.[14−21] The fluxional mechanism proposed by Adams and Cotton[17] has been widely acknowledged as being the pathway for interconversion of the isomers in solution. The *cis* and *trans* carbonyl-bridged isomers interconvert rapidly on the appropriate time scale in ^{13}C NMR spectra at ambient temperature. Because bridging−terminal carbonyl exchange is rapid for the *trans* isomer at all accessible temperatures, at ambient temperature a single averaged carbonyl resonance is observed. At lower temperatures the isomerization process is frozen into the slow limit, and separate resonances are observed for bridging and terminal carbonyls of the *cis* isomer. Adams and Cotton stipulate a low activation barrier to the bridge-opening−bridge-closing mechanism in the *trans* isomer, and Farrugia[20] showed that carbonyl exchange in the unbridged form of the *cis* isomer has a greater activation energy than the alternative pathway of scrambling through isomerization to the *trans* form. Both *cis* and *trans* isomers of [(η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$] can be crystallized, and ^{13}C NMR studies show that the carbonyl ligands are not dynamic at any accessible temperature.[22,23] The present study reports dynamics in a solid-state inclusion environment, which represents a different dynamic regime in comparison with both solution and crystalline situations.

Results

Using the standard method of Harada et al.[24−29] the 1:1 inclusion complex of γ-cyclodextrin with [(η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$] (**1**) was straightforwardly obtained. Elemental analysis supports a 1:1 cyclodextrin to metal carbonyl complex ratio. Evidence of the incorporation of the complex into the cyclodextrin is confirmed by IR analysis, which shows similar carbonyl patterns for the pure complex and the inclusion compound (Supporting Information). This article reports a detailed study of this inclusion complex through ^{13}C CP/MAS NMR spectroscopy.

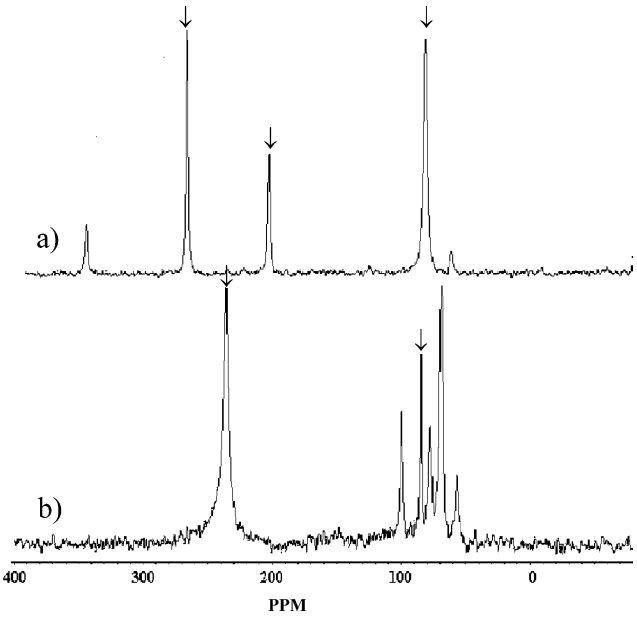

Figure 1. Ambient-temperature ^{13}C CP/MAS NMR spectra of (a) crystalline *trans*-[(η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$] and (b) [(η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$] included in γ-cyclodextrin (isotropic peaks of the organometallic are indicated by ↓).

Figure 1 shows the room-temperature (298 K) ^{13}C CP/MAS NMR spectra, recorded under identical conditions, of (a) a ^{13}CO-enriched sample of crystalline *trans*-[(η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$] and (b) its inclusion complex with γ-cyclodextrin.

For the inclusion complex of **1**, a broad resonance centered at 234.3 ppm is observed for the carbonyl groups and a single resonance at 88.3 ppm for the cyclopentadienyl carbons. The remaining resonances at 100.5, 73.3, and 60.0 ppm are attributable to γ-cyclodextrin. In contrast crystalline *trans*-**1** shows separate terminal (ca. 211 ppm) and bridging (ca. 270 ppm) carbonyl resonances, with first-order spinning sidebands clearly observed. The spinning sideband manifold allowed Aime et al.[22,23] to calculate substantial chemical shift anisotropies (CSAs) for the bridging and terminal carbonyl resonances (spans of ca. 450 and 150 ppm, respectively) of both *cis* and *trans* isomers of **1**. However, even at a MAS rate of 2 kHz, no spinning sidebands are found for the carbonyl resonance in the spectrum of the inclusion compound, demonstrating a very small CSA.

The spectrum of **1** as a crystalline specimen is largely invariant with temperature in the range 133−293 K. Conversely, as the temperature is altered for the inclusion compound, the spectrum changes significantly, as shown in more detail for the isotropic carbonyl region in Figure 2. The carbonyl peak initially broadens, and by 273 K a new, much broader peak at similar chemical shift is additionally apparent. As the temperature is

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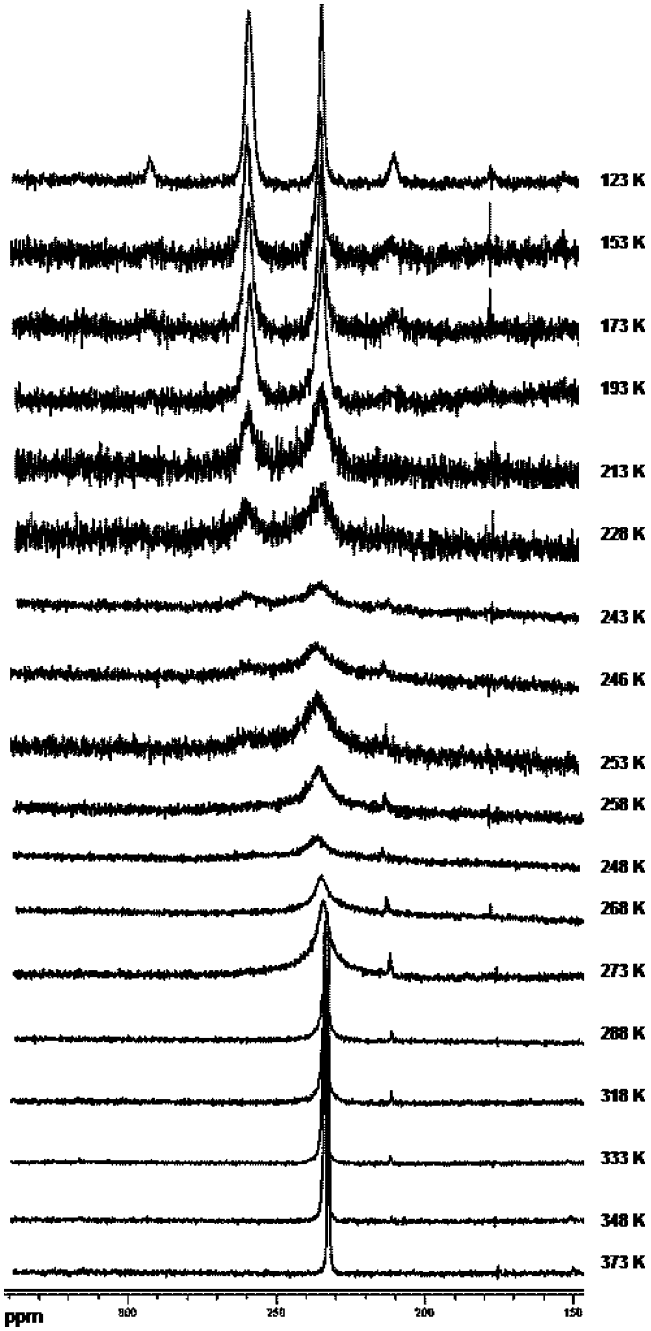

Figure 2. Isotropic carbonyl region of the VT ^{13}C CP/MAS NMR spectra of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$ in γ-cyclodextrin.

further lowered, this broad peak separates into two new peaks at ca. 210 and 270.5 ppm, which clearly can be assigned to terminal and bridging carbonyl groups, respectively. These peaks are relatively broad and at lower temperatures progressively increase in intensity, though not at the complete expense of the peak at ca. 234 ppm. The "averaged" carbonyl peak at 234.3 ppm in the ambient-temperature spectrum appears to be present at all temperatures. Its line width shows some temperature-dependence; on increasing the temperature $\Delta\nu_{1/2}$ varies from 97.3 Hz below 153 K, increasing to a maximum of 224.5 Hz at 302 K, and narrowing to 75.4 Hz by 373 K. Below about 150 K the spectral changes cease, and the spectrum contains three isotropic carbonyl peaks. That at ca. 210 ppm appears, in the isotropic region of the spectrum shown in Figure 2, to be weaker than the others, but does in fact show significant intensity in first-order spinning sidebands. The spectral features described above are clearly consistent with dynamic behavior of the guest molecules of **1**. The presence of both bridging and terminal carbonyl groups in included molecules of **1** was confirmed by the IR spectra recorded at room temperature (Supporting Information). The full interpretation of any temperature-dependence of the appearance of the cyclopentadienyl resonance at 88.3 ppm is obscured to some extent by the resonances of the cyclodextrin carbons, but any changes appear not to be dramatic.

Analysis

The single carbonyl resonance observed at 234.3 ppm in the room-temperature ^{13}C CP/MAS NMR spectrum of **1** included in γ-cyclodextrin is a clear indication of a highly fluxional system. Moreover the lack of a spinning sideband pattern is further evidence of the efficient averaging of the chemical shift anisotropy by extensive mobility of the molecules inside the cyclodextrin cavities.

Comparison of the VT ^{13}C CP/MAS NMR spectra with VT ^{13}C NMR spectra obtained in solution[14−21] indicates some similarities. Specifically, a single averaged carbonyl peak is observed at ambient temperature, and three peaks, assigned to bridging, averaged, and terminal environments, are observed at lower temperature (though this limiting spectrum is reached only at lower temperatures in the case of the solid inclusion compound). This suggests that the intramolecular fluxional processes clearly demonstrated by the solution studies and delineated through line shape analysis, namely, rapid terminal−bridging carbonyl exchange for the *trans* isomer at all accessible temperatures and *cis*−*trans* isomerization, might also occur for **1** included in γ-cyclodextrin in the solid state. Analysis of the solid-state NMR spectra must also consider the possible time scale of any overall reorientation of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$ molecules inside the γ-cyclodextrin. Of course, in solution the molecular reorientation is always in the fast regime and is not an issue in spectral interpretation. In MAS NMR spectra, any molecular reorientation that averages the CSA significantly may cause temperature-dependent broadening of the resonances, as the rate of dynamics matches the MAS rate.[30]

Complete intramolecular ligand exchange (i.e., *cis*−*trans* isomerization and terminal−bridging carbonyl exchange) at a rate fast on the exchange-broadening and CSA time scales would result in a single carbonyl resonance with such an extensively averaged ^{13}C CSA that no spinning sidebands would be expected given the present experimental conditions, as was found for example in the case of $Fe_3(CO)_{12}$.[31]

The assignment for the low-temperature ^{13}C CP/MAS NMR spectra of the inclusion compound is based mainly on the ^{13}C solution-state spectrum and the ^{13}C CP/MAS NMR data of polycrystalline samples of *cis* and *trans* isomers of **1**. This assignment is not straightforward due to the small chemical shift difference between *cis* and *trans* isomers, but further insights can be obtained if one considers the lower activation energy in solution for the bridging−terminal carbonyl exchange in the *trans* isomer.[20] The carbonyl resonances observed at ca. 270.5 and 210.2 ppm can be considered to arise from the terminal and bridging carbonyl ligands, respectively, of the *cis* isomer, whereas the signal at 234.3 ppm represents the averaged resonance for the rapidly exchanging carbonyls of the *trans* isomer. Therefore we conclude that, even at 123 K, the rate of bridge−terminal carbonyl exchange is rapid on the exchange-broadening

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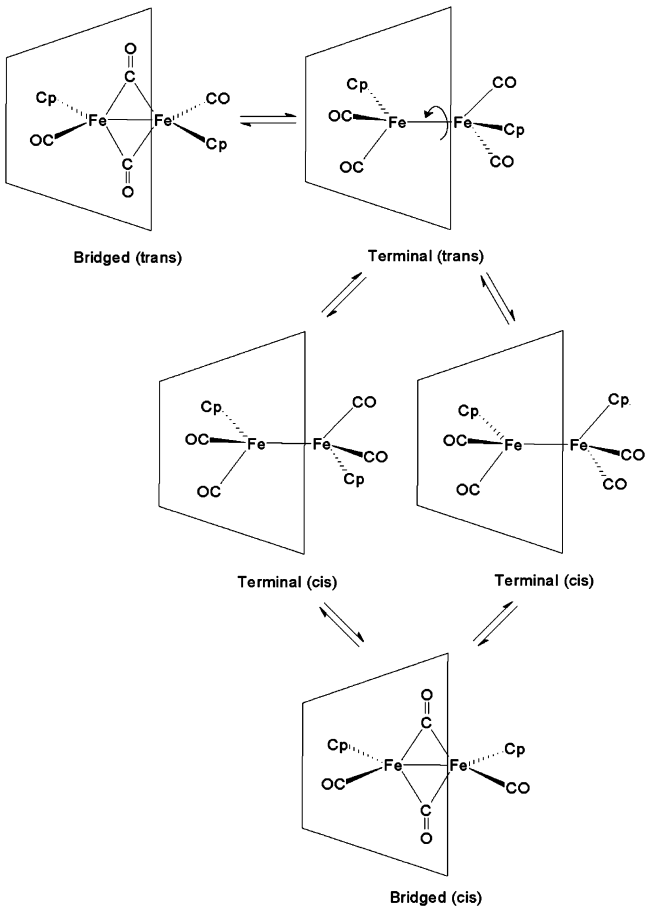
time scale; the activation barrier to this process must be surprisingly low (E_a < 25 kJ mol^{-1}), but the rate of *cis*−*trans* isomerization is clearly insignificant on the relevant time scale.

In dichloromethane solution at 243 K, the relative intensities of the three carbonyl resonances indicate a substantially higher abundance of the *cis* isomer,[14−21] as dictated by the polarity of the solvent. In the cyclodextrin inclusion compound a relatively greater abundance of the *trans* isomer is observed, as might be expected since the microenvironment provided by the cyclodextrin cavity is effectively nonpolar. The advantage to the analysis of the solution NMR line shapes of this situation is that Farrugia[20,21] was able to show with line shape analysis and magnetization transfer experiments that, despite the low equilibrium concentration of the *trans* form, the rate of terminal−bridging exchange in the *cis* isomer is determined solely by the rate of *cis*−*trans* isomerization, acknowledging the rapid rate of direct terminal−bridging exchange in the *trans* isomer.

At a qualitative level, the more rapid rate of *cis*−*trans* isomerization than direct terminal−bridging exchange in the *cis* isomer in solution is evident from differential line-broadening effects; the averaged peak of the *trans* carbonyls broadens more rapidly than do the peaks due to bridging and terminal carbonyls of the *cis* isomer in the process that leads ultimately to the coalescence of all of the carbonyl resonances. The ^{13}C CP/MAS NMR line shapes show exactly the opposite situation, where the broadening of the bridging and terminal carbonyl resonances of the *cis* isomer is extremely significant and the averaged peak of the *trans* carbonyls only broadens slightly and at temperatures in the higher temperature range of the observed dynamic effects. Clearly the spectra of **1** included in γ-cyclodextrin show demonstrably for the first time that direct terminal−bridging exchange is possible for the *cis* isomer of [(η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$] (see Scheme 1).

Scheme 1



For various reasons it is not easy to perform a detailed line shape analysis of the exchange-broadened line shapes with a view to extracting kinetic parameters for the two activated processes responsible for the spectral changes. First, the coalesced resonance for the *cis* isomer has a chemical shift similar to the averaged carbonyl resonance of the *trans* isomer, which is always present in the spectrum. Second, because the coalesced line shape of the *cis* carbonyls is very broad in the regime of interest, the line width of the averaged carbonyl resonance of the *trans* isomer is the only reliable indicator of *cis*−*trans* isomerization, and the changes in this line width are only really apparent in the higher temperature regime of the line shape changes and are not significantly distinct as to allow unambiguous determination of the rate of isomerization at any temperature. Third, as the averaging occurs at progressively higher rates, the significant CSA of static carbonyls is averaged, which affects the line widths on a time scale determined by the MAS rate and which alters the relative intensity of an isotropic peak and its sidebands. In particular, it is noticeable that the isotropic peak of the terminal cabonyl of the *trans* isomer is of particularly low intensity at low temperature (e.g., 173 K), because the large CSA of this resonance means that much of its intensity is distributed into spinning sidebands; indeed the downfield first-order sideband is of higher intensity than the center band. The bridging carbonyl resonance has a much smaller CSA and so has a higher intensity in the isotropic peak. It also appears to have an inherently more intense peak, possibly due to a shorter T_{CH} cross relaxation time in the cross polarization process. However, inspection of the spectrum at 243 K shows that just before coalescence is reached the spectral intensities of terminal and bridging carbonyl peaks are much more similar. Fourth is the issue of whether a single rate can be assigned to each dynamic process at any given temperature. One feature of note in the spectra is that at all temperatures, and especially below ambient temperature, the carbonyl resonances are surprisingly broad. The relative broadness of the carbonyl resonances appears to be largely temperature-independent—this is especially evident in the low-temperature regime below 193 K—suggesting that the measured line width represents an environmental inhomogeneity. Because of the probable inhomogeneity of the inclusion environment of molecules of **1**, it is reasonable to assume that the dynamic events will reflect a range of rates at any given temperature, because the activation parameters for the dynamic processes will depend on the exact nature of the local environment.

Discussion and Conclusions

This study constitutes an interesting new facet of a question that has been the subject of much previous effort.[14−21] Central to the detailed study of the fluxionality of [(η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$], a textbook paradigm of fluxional systems, has been the issue of whether direct terminal−bridging carbonyl interchange is possible in the *cis* isomer without isomerization to the *trans* form. The most detailed measurements show that this information is not accessible from solution studies. It is also not accessible from study of crystalline *cis*-[(η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$], because this is not fluxional. Fortuitously, the environment provided to [(η^5-C_5H_5)$_2$Fe$_2$(CO)$_4$] by γ-cyclodextrin in the solid inclusion compound permits fluxionality, but the "host−guest" intermolecular forces appear to hinder *cis*−*trans* isomerization more than they do terminal−bridging carbonyl interchange. It

is now possible to answer the key question. Direct terminal−bridging carbonyl interchange is possible in the *cis* isomer. It is not, however, possible to determine whether the exchange occurs in a concerted manner or through a nonbridged intermediate. At the lower temperatures where fluxionality involving the carbonyls of the *cis* isomer is observed, a potential unbridged intermediate, which would be common to both terminal−bridging carbonyl exchange and *cis*−*trans* isomerization processes, might have a higher barrier to the latter process because of the shape of the γ-cyclodextrin cavity and the unfavorable atomic contacts thereby engendered. It is equally plausible that the shape of the γ-cyclodextrin cavity disfavors the production of an unbridged intermediate, which slows *cis*−*trans* isomerization and its attendant carbonyl scrambling, allowing the signature of direct terminal−bridging carbonyl exchange of the *cis* isomer through a concerted process to be observed. In this second scenario the barrier measured for direct terminal−bridging carbonyl exchange of the *cis* isomer might be directly equated with the electronic barrier for concerted exchange and therefore would be a relevant barrier in fluid phases too. A further aspect of the kinetics and mechanism of fluxionality of $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$ is also further illuminated by this study, namely, the rate of terminal−bridging carbonyl exchange in the *trans* isomer. This process has not been "frozen-out" in solution, and even in a relatively high field (100.6 MHz) spectrum at 123 K it is not frozen out for the solid γ-cyclodextrin inclusion compound. In terms of the intrinsic electronic barrier this must indeed be an extremely facile process. Yet by the same token the barrier to exchange is evidently exquisitely—surprisingly so—sensitive to the nature of the intermolecular forces on the molecule, because there is no evidence of exchange in pure crystalline *trans*-$[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$. This study acts as a paradigm for how selection of an inclusion environment for a guest molecule can allow the "engineering" of a specific set of circumstances to favor the study of certain aspects of the molecule's behavior that are not accessible in solution or simple crystalline situations. Also it is a very clear illustration of how study by solid-state NMR spectroscopy of molecular dynamic behavior may illuminate, in a detailed fashion, aspects of structure in materials, such as these inclusion compounds, which are not amenable to study by diffraction techniques.

Although the present study did not have a planned outcome, it raises the possibility that as understanding of the influence of the interplay of intermolecular interactions on the structure and dynamics of molecules in the solid state improves, it may be possible to "engineer" solid-state environments for a given molecule that are designed to influence the balance between different dynamic processes or structural influences in order to achieve a specific outcome, such as selectively hindering one dynamic process in order to make study of another one possible.

Experimental Section

Preparation of Cyclodextrin Inclusion Compounds of Metal Carbonyls.[24−29] The "host−guest" inclusion compounds were prepared following the method originally proposed by Harada et al.[24] for ferrocene in cyclodextrins. $[(\eta\text{-}C_5H_5)_2Fe_2(CO)_4]$ in finely powdered form was added to a stirred saturated solution of γ-cyclodextrin in distilled water, maintained at 60 °C for 8−12 h. $[(\eta\text{-}C_5H_5)_2Fe_2(CO)_4]$ and γ-cyclodextrin were used as supplied by Aldrich. The complex/cyclodextrin molar ratio used was 2:1 (this maximizes yield with respect to the expensive labeled guest compound). The precipitate was collected by centrifugation, then washed with three aliquots of distilled water to eliminate any free cyclodextrin component and with three aliquots of benzene to remove the unincluded carbonyl compound. A final washing with water produced the desired inclusion compound. The high solubility of γ-cyclodextrin in water makes yields rather variable, but unincluded cyclodextrin and metal carbonyl could be recovered and recycled.

Elemental analysis was performed by the Analytical Service of the Inorganic Chemistry Laboratory, University of Oxford, using combustion for C and H, and ICP-AES for Fe and Mo. Anal. Found: Fe, 6.09; C, 42.00; H, 5.81. Calcd for γ-cyclodextrin−$[(\eta\text{-}C_5H_5)_2Fe_2(CO)_4]$−$(H_2O)_x$: Fe, 6.09; C, 42.00; H, 5.81.

^{13}C-Enrichment. ^{13}CO-enriched $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$, with about 20% ^{13}C enrichment, was prepared by direct exchange of ^{13}CO with the appropriate metal carbonyl in heptane (purified by standard techniques[32]) solution at 80 °C for 3 days.[33] ^{13}CO (99% enriched) was purchased from Isotec, Miamisburg, OH.

Solid-State NMR Spectroscopy. ^{13}C CP/MAS NMR spectra were acquired on a Varian Chemagnetics CMX Infinity 400 (9.4 T) instrument operating at 100.6 and 400.26 MHz for ^{13}C and ^{1}H, respectively. Figure 1a was acquired on a JEOL GSX 270 WB. Samples were packed in 4 mm zirconia rotors using Teflon spacers to provide a typical sample volume of 100 μL. MAS rates varied from 2 to 14 kHz and are quoted where appropriate in the text and in figure legends. Cross polarization was performed with a single contact X-ramped sequence, utilizing a 2.4 μs ^{1}H 90° pulse and an 83 kHz ^{1}H rf-decoupling field. Typically 256−512 transients were collected for each spectrum with a delay between transients of ca. 20 s.

IR Spectroscopy. IR spectra were recorded on a Bruker FT-IR spectrophotometer model Equinox 55.

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Supporting Information Available: IR spectra of solid $[(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4]$ and its host−guest inclusion complex with γ-cyclodextrin. This material is available free of charge via the Internet at http:/pubs.acs.org.

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