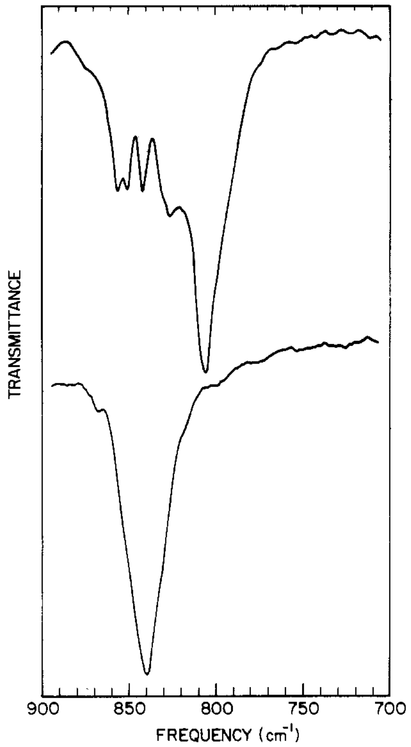

Figure 4. Infrared spectra of the perpendicular C–H bending region obtained at room temperature on KBr pellets of unoxidized neutral form of **2** (top) and the triiodide salt of **2** (bottom).

drawing group, increasing the oxidation potential of a ferrocene. For example, the oxidation potential of acetylferrocene is 0.790 V (vs. SCE) compared to 0.540 V for unsubstituted ferrocene.[7] The introduction of a single acetyl substituent on **1** to give **2** could lead to an appreciable zero-point energy difference between the two different vibronic states for **2**.

Contrary to our simple expectations, we found that the mixed-valence cation **2** has a delocalized ground state. A single quadrupole-split doublet is seen at 4.5 K in the Mössbauer spectrum for the triiodide salt of **2**. The EPR spectra for the triiodide salts of **1** and **2** look very similar, but quite different from the EPR spectra seen for EPR-localized mixed-valence biferrocenes. The IR spectrum and intensity of IT band for the triiodide salt of **2** also point to a delocalized ground electronic state for **2**.

The observation that the single unpaired electron in cation **2** is delocalized over both halves of the molecule indicates that the electron-withdrawing nature of the acetyl substituent has had little effect on the electronic structure of the bis(fulvalene)diiron cation. This very likely results from the fact that there is a strong electronic coupling between the electronic manifolds of the two iron ions in both **1** and **2**. There is no barrier for electron transfer. The single unpaired electron in **2** is located in a molecular orbital that has comparable contributions from both metallocene moieties.

In fact, the very recent report by Hillman and Kvick[14] of the X-ray structure of the picrate hemihydroquinone salt of **1** indicates the nature of the strong Fe–Fe electronic coupling in **1** and **2**. They found that the Fe–Fe distance (3.636 (1) Å) in mixed-valence **1** is 0.35 Å shorter than in the corresponding neutral Fe_2^{II} complex. The bis(fulvalene)diiron framework distorts upon oxidation to **1** so as to increase the direct Fe–Fe interaction in the mixed-valence cation. Such a direct Fe–Fe interaction had previously been suggested[8] as the explanation for the diamagnetism of the dioxidized Fe_2^{III} analogue of **1**. Apparently a direct Fe–Fe interaction is maintained in **2**, and this explains why the acetyl substituent does not have much effect on the extent of delocalization.

Acknowledgment. We are grateful for support from NIH Grant HL13652.

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Matrix-Isolation Study of Oxide-Transfer Reactions to Halogen-Containing Lewis Acids: Synthesis of the $CO_2F_2^{2-}$ Anion and Attempted Synthesis of the BF_3O^{2-} Anion

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The oxide-transfer technique has been coupled with matrix isolation in an attempt to synthesize and characterize the BF_3O^{2-} and $CO_2F_2^{2-}$ anions, through the reaction of Tl_2O with either BF_3 or COF_2. In the latter experiments, two sets of product bands were observed; one agreed well with the absorptions of the known CO_2F^- anion. The second set has been assigned to the $CO_2F_2^{2-}$ anion in the matrix-isolated $Tl^+{}_2CO_2F_2^{2-}$ triple ion, which rapidly eliminated TlF upon warming to form the $Tl^+CO_2F^-$ anion. Attempts to synthesize the BF_3O^{2-} anion in a similar fashion were not successful, suggesting that previous reports of the room-temperature synthesis of this anion are incorrect.

Introduction

The salt/molecule technique[1] was developed 10 years ago for the synthesis of unusual and highly reactive anions in inert matrices. This technique was initially employed for the transfer of a halide anion to a variety of Lewis acids to form the desired anion in a matrix-isolated ion pair.[2–6] Recently, the oxide-transfer technique[7] was developed in which an oxide anion O^{2-} is transferred from Tl_2O to a suitable acceptor, to form an oxyanion in a matrix-isolated triple ion. Species that have been formed in this manner[7–9] include CO_3^{2-}, CO_2S^{2-}, COS_2^{2-}, SO_3^{2-}, and $S_2O_5^{2-}$. A direct, and important, extension of this technique would be to the reaction of Tl_2O with halogen-containing Lewis acids such as BF_3 and COF_2. For these systems, not only is the addition reaction feasible to form the product oxyanion, but a variety of elimination reactions may occur to form further products.

The synthesis of the BF_3O^{2-} anion was the first reported in the late 1950s, and spectroscopic characterization followed thereafter.[10–14] However, since that time researchers have demon-

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strated that this anion was not formed, but impurities were responsible for the observed spectra.[15,16] A similar disagreement surrounds the purported synthesis of the $CO_2F_2^{2-}$ anion, where one group[17] claimed to have formed this anion but another group was not able to repeat the synthesis.[18] If either of these 32-electron species are stable entities, the matrix-isolation technique should provide perhaps the best chance for characterization. The oxide-transfer reaction from Tl_2O to either BF_3 or COF_2 provides the most likely avenue to the matrix synthesis of these anions. Consequently, a matrix investigation of the reactions of Tl_2O with BF_3 and COF_2 was undertaken, to gain insight into the stabilities of these anions, as well as to determine the range of applicability of the oxide-tranfer technique.

Experimental Section

All of the experiments carried out in this study were done on a matrix-isolation system that has been described previously.[19] Tl_2O was the only metal oxide employed, as all of the alkali-metal oxides have been shown to decompose prior to vaporization. In addition, Tl_2O is known to vaporize without decomposition, in a temperature range accessible with the current equipment, and vaporizes to yield primarily monomeric Tl_2O, with some dimeric species.[20,21] BF_3 (Matheson) and COF_2 (PCR Research Chemicals) were handled in a stainless-steel vacuum line and subjected to one or more freeze–thaw cycles at 77 K prior to sample preparation. BF_3 tended to adsorb on the walls of the vacuum line, and it was difficult to prepare a sample of accurately known concentration. Argon was used as the matrix gas in all experiments and was used without further purification.

Matrix samples were generally deposited at 2 mmol/h for 20–24 h, while the $Tl_2O(s)$ was heated to approximately 430 °C, where it is known to have about 1 μm vapor pressure. The effusing $Tl_2O(g)$ was codeposited with the Ar/BF_3 or Ar/COF_2 samples. Spectra were recorded on a Perkin-Elmer 983 infrared spectrometer with computer data station. As will be described below, at the end of each experiment, the refrigerator was turned off and the cold window warmed to room temperature. During this process, the $Tl_2O(s)$ in the Knudson cell was necessarily exposed to the vaporized matrix, i.e. to gaseous BF_3 or COF_2, and some surface reactions were apparent in subsequent spectra.

Results

Before the reaction of BF_3 or COF_2 with Tl_2O was investigated, blank experiments were conducted on each of the reactants alone in argon. In each case, the spectra were in good agreement with literature spectra[22,23] and with blank experiments conducted previously in this laboratory.[24]

$Tl_2O + COF_2$. Tl_2O was vaporized over a range of oven temperatures, from approximately 420 to 500 °C and codeposited with samples of Ar/COF_2 (M/R) with dilutions ranging from 500/1 to 2000/1. As noted in previous studies,[8] the variation in oven temperature caused a variation in the temperature of the cold window of approximately 4 K, which in turn had some effect on the products formed. When Tl_2O was vaporized at a relatively low oven temperature, and hence a relatively low cold window temperature, and codeposited with a sample of Ar/COF_2 = 2000, new infrared absorptions were noted at 442, 612, 700, 885, 930, 1324, 1382, and a doublet near 1700 cm^{-1}. These bands were quite sharp, and the bands at 1324, 1382, and 1700 cm^{-1} were moderately intense. When this sample was annealed to 35 K and then recooled to 14 K, the bands at 442, 885, 1324, and 1700 cm^{-1} grew in intensity, while the bands at 612, 700, 930, and 1382 cm^{-1} decreased in intensity.

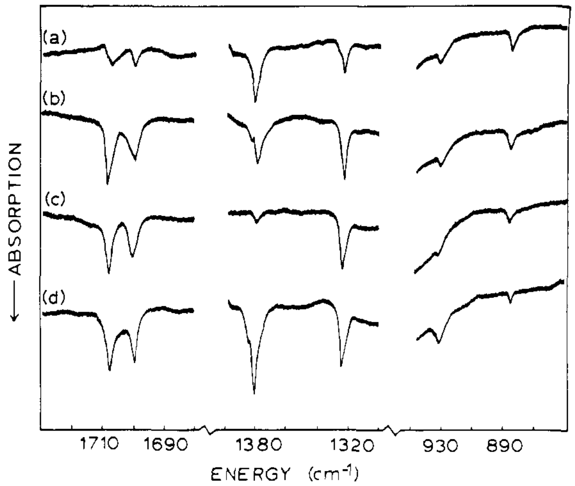

Figure 1. Infrared spectra of the reaction products arising from the codeposition of Tl_2O with samples of Ar/COF_2. Trace a depicts the reaction of M/R = 1000 and a cold window temperature of 14 K, while trace b shows the same sample after annealing to 35 K and recooling. Trace c shows the spectrum from the codeposition of Tl_2O with Ar/COF_2 = 1000 and a cold window temperature of 18 K, while trace d shows a more highly concentrated sample, Ar/COF_2 = 500, but with a cold window temperature near 14 K.

In a subsequent experiment, Tl_2O was vaporized at 500 °C (cold window temperature near 18 K) and codeposited with a similar sample of Ar/COF_2 = 2000. Under these conditions, the same set of product bands was noted, but the relative intensities were altered. The bands at 442, 885, 1324, and 1700 cm^{-1} were relatively more intense (hereafter called set one) while the bands at 612, 700, 930, and 1382 cm^{-1} (hereafter called set two) were relatively less intense than in the above experiment. To the degree to which intensities could be measured (the bands at 612 and 700 cm^{-1} were always quite weak), the relative intensities *within* a set of bands (set one or set two) were the same in both experiments. Additional experiments were conducted at M/R values of 1000 and 500; similar results were obtained throughout, namely that two sets of bands were present and that somewhat higher vaporization or cold window temperatures led to increased yield of set one and decreased yield of set two, as can be seen in Figure 1. Finally, Tl_2O was vaporized and codeposited in a number of experiments with samples of either $Ar/COClF$ or $Ar/COCl_2$. No product bands were noted in any of these experiments.

$Tl_2O + BF_3$. When these two reactants were codeposited in an initial experiment at a dilution of 500/1, no new absorptions were observed that could not be attributed to either parent species. However, as a series of experiments was conducted over a concentration range from M/R = 2000 to 500, new peaks began to appear in the spectrum in the 900–1000- and 1180–1260-cm^{-1} regions. These peaks were never particularly intense, and their relative intensities varied from one experiment to the next. In addition, a sharp, moderately intense band began to appear at 442 cm^{-1}, as had been observed in the above experiments with COF_2.

To test the possibility that these bands arose from surface reaction products when gas-phase BF_3 was exposed to the Tl_2O solid surface within the oven, a new branch of Tl_2O was loaded into the oven and an additional blank experiment was conducted. The spectrum thus obtained was consistent with earlier blank experiments of Tl_2O in argon. The solid sample within the oven was then intentionally exposed to several torr of BF_3 for several minutes, before the vacuum vessel was evacuated to 10^{-6}–10^{-7} torr. The oven was then heated to the usual Tl_2O deposition temperatures, and the growth of a number of weak bands in the 1200-cm^{-1} region was observed, along with the band at 442 cm^{-1}. In every subsequent experiment using this batch of Tl_2O these bands were present.

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In a series of experiments, metallic thallium was also codeposited with samples of BF_3 in argon. Initially, no reaction was observed, and no new product bands appeared in the spectra. However, after the Tl(s) was exposed to gas-phase BF_3 and subsequent experiments were carried out, the band at 442 cm^{-1} began to appear, along with a broad triplet in the 1200–1340-cm^{-1} region. Finally, TlF was loaded into the oven, vaporized, and codeposited with a sample of $Ar/BF_3 = 500$. This pair of reactants has been studied previously[25] and is known to yield the $Tl^+BF_4^-$ ion pair, with absorption at 1072,, 1188, and 1225 cm^{-1}. These bands were detected in the present study, along with weak absorptions in the 1220–1240-cm^{-1} region.

Discussion

The codeposition of Tl_2O with COF_2 into argon matrices gave rise to a number of sharp, well-defined infrared absorptions; the diffusion and thermal behavior of these bands indicated a separation into two distinct sets. The first, typified by bands at 885, 1324, and 1700 cm^{-1}, was favored at relatively high cold window temperatures and after annealing of the matrix. In addition, when these bands grew in intensity, a band at 442 cm^{-1} was noted to grow at the same rate. This band at 442 cm^{-1} has been observed in a number of previous matrix experiments[25,26] and has been assigned to monomeric TlF. This material can be vaporized directly, and the spectrum obtained in this manner agrees precisely with the 442-cm^{-1} band observed here (although when it is vaporized from the solid, dimeric and polymeric TlF is observed as well). The growth of this first set of bands along with a growth in TlF is suggestive of an elimination reaction, where some initial product eliminates a molecule of TlF; presumably the initial reaction product is characterized by the second set of bands, primarily those at 930 and 1382 cm^{-1}, which decreases upon annealing.

The first set of bands matches within a few wavenumbers the three most intense bands of the fluoroformate anion CO_2F^-, which has been identified previously in argon matrices.[27] In this earlier study, the metal cation was Cs^+, and since band positions are known[2] to move slightly with a change in cation, a shift of a few wavenumbers is readily understood. Given the chemical composition of the initial reactants, the concurrent growth of the TlF absorption, and the known stability of the CO_2F^- anion in isolated ion pairs, the assignment of the first set of product bands to the $Tl^+CO_2F^-$ ion pair is quite reasonable.

With identification of the first set of bands as due to the $Tl^+CO_2F^-$ ion pair and the knowledge that TlF grows in as this species is formed during annealing, the initial reaction product is indicated as having the overall formulation $Tl_2CO_2F_2$, as would be formed from an initial 1/1 reaction of Tl_2O with COF_2. However, whether this species is best represented as a distinct $CO_2F_2^{2-}$ anion in the $Tl^+{}_2CO_2F_2^{2-}$ triple ion or whether the species is a more loosely bound molecular complex is less readily apparent. Two distinct infrared absorptions, at 930 and 1382 cm^{-1}, and two weak absorptions, near 612 and 700 cm^{-1}, provide the only indication of the structure of the product. If the complex is a loosely bound molecular adduct, the perturbation to each of the subunits in the complex would be relatively small, whereas the formation of a distinct anionic product would provide a much more dramatic shift. For example, the reaction of CsF with COF_2 yields the COF_3^- anion,[28] and the C–O stretching mode shifts over 400 cm^{-1}, from near 1950 cm^{-1} in COF_2 to 1514 cm^{-1} in COF_3^-. The observation of a moderately intense band at 1382 cm^{-1} is indicative of a large perturbation to the COF_2 unit (presumably this band represents a perturbation to the C–O stretch rather than to the antisymmetric C–F stretch, as a shift *upward* of over 100 cm^{-1} is very unlikely); certainly, perturbation of the Tl_2O subunit could not lead to such a band. $CO_2F_2^{2-}$ is isoelectronic with COF_3^-, which suggests that the former ion might be stabilized *and* that it should have its antisymmetric C–O stretching vibration in the 1400–1500-cm^{-1} region. With the additional negative charge on the $CO_2F_2^{2-}$ anion relative to COF_3^-, a shift to 1400 cm^{-1} or below is likely and the 1382-cm^{-1} band is a good candidate for the more intense, antisymmetric C–O stretching mode. The second most intense band for this anion would be the antisymmetric C–F stretching mode. By analogy to both COF_3^- and CO_2F^-, this mode should lie near 900–950 cm^{-1}, which matches well the observed 930-cm^{-1} absorption. The antisymmetric C–F stretching mode of parent COF_2 lies near 1250 cm^{-1}, and this large shift to 930 cm^{-1} is also indicative of a strong perturbation and added electron density. These arguments collectively suggest that the initial reaction product between Tl_2O and COF_2 is of the formulation $Tl_2CO_2F_2$, that it is primarily ionic, and that can be represented reasonably well as the $CO_2F_2^{2-}$ anion in the $Tl^+{}_2CO_2F_2^{2-}$ triple ion. The elimination of the relatively ionic TlF and formation of the $Tl^+CO_2F^-$ ion pair upon annealing or higher cold window temperatures is certainly consistent with this formulation. This behavior in the 14–35 K temperature region also points out the very limited stability of the $CO_2F_2^{2-}$ anion with respect to TlF elimination. Hence, it is not surprising that attempts[18] to synthesize this anion at room temperature have been unsuccessful. Nonetheless, under these extremely low-temperature conditions the $CO_2F_2^{2-}$ anion appears to have some limited stability. Martineau and Milne[17] did report partial infrared spectra of the compound that they identified as $Cs_2CO_2F_2$. However, they noted that their compound was very hygroscopic, and obtaining infrared spectra was very difficult. In view of the disagreement of their bands with those observed here and the highly hygroscopic nature of their species, it is likely that the infrared spectra obtained were of a hydrolysis product rather than $Cs_2CO_2F_2$.

By comparison, the results from the codeposition of Tl_2O with BF_3 into argon matrices are less conclusive. In the initial experiments, no product bands were noted, while in later experiments a number of weak absorptions were noted in the 1200-cm^{-1} region. However, most of these could be reproduced by exposing solid Tl_2O in the oven to gaseous BF_3 and then heating the Tl_2O. In addition, all of these subsequent experiments showed a moderately intense band at 442 cm^{-1}, which, as above, is assigned to TlF. This indicates that surface reaction and/or decomposition is occurring, in contrast to the initial experiments where the reactants were "clean" and no products were observed. Certainly, adsorption of BF_3 on a solid surface capable of donating electrons is well-known.[29-31] These data suggest that BF_3 and Tl_2O do *not* react in an isolated sense to form the BF_3O^{2-} anion. Whether this lack of reaction is kinetic in nature, with a high barrier to reaction, or whether it is thermodynamic in nature cannot be determined from these experiments. The study of Long and Bailey[14] on the BF_3O^{2-} anion did report several infrared absorptions for this species, including strong bands at 827, 1085, and 1360 cm^{-1}. These, however, were later assigned to the impurity species $Zn(NO_3)_2$ and $ZnSiF_6$ in their samples.[16] These bands do not match those observed here, and as the chemical approaches to this system were quite different, this is not surprising. Nonetheless, formation of the BF_3O^{2-} anion under low-temperature matrix-isolation conditions is not indicated. In view of the limited stability of the $CO_2F_2^{2-}$ anion and the ease by which it eliminates TlF, the lack of observation of the BF_3O^{2-} anion under these conditions casts considerable doubt on the early reports of the room-temperature synthesis of this anion. Certainly, the later reports the zinc nitrate and fluorosilicate accounting for all of the observations very likely yield the correct interpretation.

Assignment of the numerous weak bands that were observed in some of these experiments is not readily done; several lie near bands of the $Tl^+BF_4^-$ ion pair. Quite possibly the surface reaction of BF_3 with Tl_2O leads to nonvolatile borates and TlF, which then vaporizes upon heating and reacts with residual BF_3 to form this

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ion pair. Other mixed fluoroborates are feasible in this system; the spectral data do not provide a means for positive identification, and indeed that was not the intent of this study.

Conclusions

The present study has provided the first spectroscopic evidence for the existence, although limited, of the $CO_2F_2^{2-}$ anion. The spectra also suggest that TlF elimination to form the Tl^+ CO_2F^- is very facile, even at the very low temperatures employed. By comparison, no evidence was found for a discrete BF_3O^{2-} anion, casting serious doubt on reports of the room-temperature synthesis of this species. Beyond these findings, this study demonstrates that the competing pathway of TlF elimination is sufficiently favored that the stabilization of mixed oxyfluoride anions of a 2− charge is difficult and in many cases not feasible. By comparison, those systems where the oxide-transfer technique was most effective in producing a distinct anionic species were those where electron delocalization could occur through a π-bonding network.[7–9]

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Electronic Structure of Ferracyclopentadienyl Derivatives. UV PES and ab Initio Study of $Fe_2(\mu\text{-}CO)(CO)_5(C_4R_4)$ and $Fe_3(\mu\text{-}CO)_2(CO)_6(C_4R_4)$

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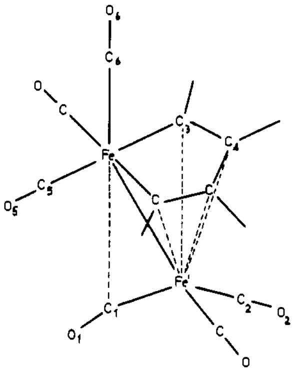
The gas-phase UV PE spectra of metallacyclopentadienyl bi- and trinuclear derivatives of Fe and Ru are reported and discussed. The bonding scheme of these molecules is discussed on the basis of theoretical results obtained by pseudopotential ab initio calculations. The role played by semibridging or asymmetrically bridging carbonyl groups has been clarified. The very high stability of the metallacyclopentadienyl ring has been ascribed to the presence of a very strong M–C interaction, only σ in character.

Introduction

It was early recognized that the major products in the reaction between iron carbonyls and alkynes are the dimerization title compounds (I and II).[2] The complexes I and II contain an identical structural arrangement of the metallacyclopentadienyl FeC_4 system, and compound II can be envisaged as the result of the addition of an $Fe'(CO)_3$ unit to the type I compound. The X-ray structure determination of $Fe_2(CO)_6[C_4(CH_3)_2(OH)_2]$, reported by Hock and Mills in 1961,[3] revealed the first example of a molecule containing a semibridging carbonyl group; it was shown that one of the CO groups exhibits an anomalous behavior since the $Fe'–C_1–O_1$ angle (see structures I and II) is only 168° and the distance between the ring Fe atom and C_1 amounts to 2.48 Å, which is rather low for two nonbonded atoms. Subsequent X-ray investigations on similar compounds showed the same peculiarity.[4] Cotton[5] proposed to interpret this behavior on the basis of electronic arguments: adopting the validity of the EAN rule, he suggested a Fe'→Fe dative bond and the consequent relief of the charge excess of Fe by back-donation to $\pi^*_{\parallel}$ of $C_1–O_1$ (hereafter $\parallel$ and $\perp$ symbols refer to the plane passing through metal atoms and bridging or semibridging carbonyls).[6] The agreement on this explanation, however, is not general since very recently[4g] some authors proposed to ascribe the bending of $Fe'–C_1–O_1$ to steric hindrance. The presence of two different types of iron atoms was also assessed by Mössbauer spectroscopy,[7] and the fluxional behavior of the $Fe'(CO)_3$ group was investigated by VT ^{13}C NMR spectroscopy.[8] It was shown that the "frozen" structure containing the semibridging carbonyl can be detected only at low temperature.



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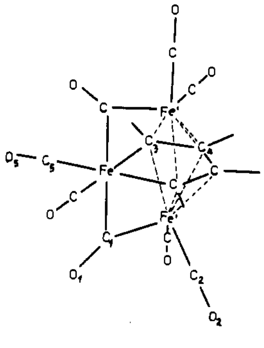

II

An X-ray determination of a type II structure was reported by Dodge et al.[9] for $Fe_3(CO)_8(C_4Ph_4)$; the metallic frame corresponds to an open triangle whose two edges are asymmetrically bridged by CO groups and the metallacycle is perpendicularly crossing the Fe_3 plane. Furthermore, the VT ^{13}C NMR spectra showed that a localized CO exchange at each $Fe'(CO)_3$ unit is occurring in the reported range of temperature.[10]

These interesting features prompted us to seek new theoretical and spectroscopic evidence in order to obtain a more detailed

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