

direct and larger perturbation will occur. From a conceptual viewpoint the outcome of the latter conjugative interaction is more easily anticipated. The extension of the π -system of S_3N^- to include the X group will naturally lead to a decrease in the energy gap between the occupied and unoccupied orbitals. Thus the red shift observed for S_4N^- and Ph_3PN-S_3N relative to S_3N^- is as expected. The smaller shift for Ph_3PN-S_3N probably reflects the higher electronegativity of a nitrogen vs. a sulfur lone pair; its mixing with the frontier π orbitals of the S_3N chromophore will be less extensive (see Figure 3). Similar trends are observed in the $\pi^* \rightarrow \pi^*$ transition energies of carbonyl²² and thiocarbonyl²³ groups possessing π -donor ligands.

In the present molecule **4** the absence of such conjugative effects allows an assessment of the first type of perturbation. While the result would be difficult to predict on an a priori basis, it is apparent that the conversion of a lone-pair orbital of S_3N^- into a C-S σ -bond in **4** leads to an increase in the π^*

$\rightarrow \pi^*$ transition energy. In the light of this result the true magnitude of the conjugative effects in X- S_3N derivatives becomes apparent. Relative to nonconjugating ligands (such as the norbornenyl group in **4**) soft π -donor ligands (such as sulfur) cause a bathochromic shift of up to 150 nm, while harder donors (e.g. nitrogen) produce somewhat smaller shifts (ca. 70 nm in Ph_3PN-S_3N).

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Supplementary Material Available: Tables of anisotropic thermal parameters (Table S1), structural parameters relating to hydrogen atoms (Table S2), and structure factor amplitudes for $C_7H_8(S_3N)_2$ (19 pages). Ordering information is given on any current masthead page.

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Interactions of *triangulo*-(μ -Carbonyl)decacarbonyl(μ -hydro)triferrate(1-), $HFe_3(CO)_{11}^-$, with Its Counteranion and Solvent

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A series of $MHFe_3(CO)_{11}$ complexes ($M = Li, Na, K, Rb, Cs$) have been synthesized, and their ion-pairing phenomena in solutions and solid state have been studied by IR spectroscopy. In ether or dioxane, all the $MHFe_3(CO)_{11}$ salts exist as contact ion pairs. The ν value of the bridging CO of $HFe_3(CO)_{11}^-$ increases in the order $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$. In THF, $MHFe_3(CO)_{11}$ exists as less associated forms and contact ion pairs. The nature of these two forms was characterized by the crown ether titration of a representative member of the series, $KHFe_3(CO)_{11}$. The ratio of the less associated forms to the contact ion pairs was determined and found to decrease in the order $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. In Me_2SO , CH_3CN , CH_3NO_2 , or diglyme, only the less associated forms were observed for all $MHFe_3(CO)_{11}$ salts. The difference in the ν values of the bridging CO of the less associated forms in different solvents is explained in terms of hydrogen bonding between the oxygen of the bridging CO and the acidic protons of the solvent molecule. The interaction between solvent and μ -CO is best seen in alcohol solutions. $MHFe_3(CO)_{11}$ also exists in two forms in alcohol. One is the "less associated form" at 1745 cm^{-1} , while the other is the "solvated form" at 1699 cm^{-1} arising from the interaction of the bridging CO and the hydroxyl group in alcohol. The nature of the solvated form is different from that of the contact ion pair, and methods for distinguishing between the two species were described. In the solid state, besides the cation-bridging CO interaction, a cation-terminal CO interaction for the potassium and rubidium salts was also inferred from the similarity of the IR spectra at the lower frequency end of the terminal CO region of these salts and $[(i-Pr)_2NH_2][HFe_3(CO)_{11}]$ and the X-ray structure determination study of the latter complex.

Introduction

There has been considerable interest in the ion-pairing phenomena of the transition-metal carbonylates¹⁻¹⁴ due to the

close relationships of the ion-pairing behaviors to the reactivities of the carbonylates. To date, the majority of the investigations were focused on mononuclear metal carbonylates.¹⁻¹² Only two works are related to the ion pairings of dinuclear and trinuclear metal carbonyl anions. In the dinuclear system $MHFe_2(CO)_8$, with $M = Li$ or Na , Collman et al.¹³ have shown that the counteranion formed a contact ion pair with the bridging carbonyl group of $HFe_2(CO)_8^-$ in THF, while in the trinuclear system $(Et_3NH)[HFe_3(CO)_{11}]$, Pribula and co-workers³ had revealed that the proton in the tri-

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Table I. ν_{CO} of the Bridging Carbonyl and the Lowest ν_{CO} of the Terminal Carbonyls of $\text{MHFe}_3(\text{CO})_{11}$ in Various Solvents and in the Solid State

salt	lowest ν_{CO} - (terminal) for solid, ^a cm^{-1}	ν_{CO} (bridging), cm^{-1}										
		solid ^a	Et ₂ O	dioxane	diglyme	Me ₂ SO	CH ₃ CN	CH ₃ NO ₂	THF		ethanol	
LiHFe ₃ (CO) ₁₁	<i>b</i>	1641	1660	1649	1740	1730	1726	1724	1745	1670	1745	1699
NaHFe ₃ (CO) ₁₁	<i>b</i>	1670	1665	<i>c</i>	1740	1730	1726	1724	1745	1690	1745	1699
KHFe ₃ (CO) ₁₁	1906	1690	1679	1678	1740	1730	1726	1724	1745	1696	1745	1699
RbHFe ₃ (CO) ₁₁	1906	1690	1681	<i>c</i>	1740	1730	1726	1724	1745	1698	1745	1699
CsHFe ₃ (CO) ₁₁	1930	1660	<i>c</i>	1686	1740	1730	1726	1724	1745	1701	1745	1699

^a In Nujol. ^b The IR absorption bands are broad in the terminal CO region, and no well-resolved peaks were observed. ^c Not measured.

ethylammonium ion formed a hydrogen bond with the oxygen atom of the bridging carbonyl group in benzene or CH_2Cl_2 . In most of these ion-pairing studies, the alkali cations used were limited to Na^+ and Li^{+2-13} due at least partly to the difficulties in the synthesis of other alkali salts. Consequently, a systematic investigation of the effects of cations and solvents on the ion-pairing behaviors is still lacking. Moreover, the interactions of solvents with carbonyl anions were overlooked and have never been explored.

In this paper, we report the synthesis of a series of alkali metal salts $\text{MHFe}_3(\text{CO})_{11}$ with $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb},$ and Cs and the results of a systematic investigation on the ion-pairing behaviors of these salts in various solvents and in solid state. Evidence for a varying degree of interaction between the bridging CO group of $\text{HFe}_3(\text{CO})_{11}^-$ anion and solvents is presented. Furthermore, the interactions between some of the cations and the terminal CO group of $\text{HFe}_3(\text{CO})_{11}^-$ in the solid state as evidenced by the IR spectra are also described.

One of the most significant aspects of the investigation is the observation of a new species that we call the "solvated form" from the interaction of $\text{HFe}_3(\text{CO})_{11}^-$ and solvent in alcohol. The nature of the solvated form is different from those of the well-established contact ion pair and the less associated form, and methods for the differentiation are given in the paper. This new type of interaction, which has not been characterized before, might also exist in other systems in polar solvents.

Owing to the complexity of the structure, a metal cluster carbonylate is expected to provide more interaction sites for its countercation than the mononuclear carbonylate. The possibility of the existence of a variety of cation-carbonyl cluster anion interactions and subsequent effects of the interactions on the reactivity and structure of the cluster anion prompted us to undertake the current study.

Experimental Section

All experiments were conducted under an atmosphere of nitrogen by using modified Schlenk techniques. ¹H NMR spectra were measured on a JEOL FX-100 and IR spectra were recorded on a Jasco 100 or a Perkin-Elmer 580 spectrophotometer. Elemental analyses were performed by Union Industrial Institute, Hsinchu, Taiwan.

Iron pentacarbonyl (Strem) and RbCl and CsCl (Merck) were used as purchased. All solvents were dried by the conventional methods and degassed before use.

Preparation of Potassium *triangulo*-(μ -Carbonyl)decacarbonyl(μ -hydro)triferrate(1-), $\text{KHFe}_3(\text{CO})_{11}$. To a 50-mL three-necked flask were added 9.6 mL of ethanol, 1.32 g (0.024 mol) of KOH, and 3.70 g (0.024 mol) of $\text{Fe}(\text{CO})_5$. The solution was then heated under nitrogen at 85 °C overnight. The solvent was removed by vacuum distillation. The crude product obtained was redissolved in THF, and the solution, after filtration to remove the undissolved material, was evaporated to afford the analytically pure product. Anal. Calcd for $\text{C}_{11}\text{HFe}_3\text{KO}_{11}$: C, 25.62; H, 0.20. Found: C, 25.23; H, 0.20. Characteristic IR bands (ν_{CO}) at 2060 (w), 1994 (s), 1975 (s), 1940 (sh), and 1726 (m) cm^{-1} in acetonitrile are identical with those of the known $(\text{HNEt}_3)[\text{HFe}_3(\text{CO})_{11}]$ and $(\text{PPN})[\text{HFe}_3(\text{CO})_{11}]$.

$\text{LiHFe}_3(\text{CO})_{11}$ and $\text{NaHFe}_3(\text{CO})_{11}$ were prepared similarly by using the corresponding alkali hydroxide as the base. However, both salts

are very air and moisture sensitive, and no elemental analysis was performed. They were readily identified by comparing their CO stretching frequencies and the chemical shift of the hydride (δ 14.94 in $\text{Me}_2\text{SO}-d_6$) with the corresponding data of $(\text{HNEt}_3)[\text{HFe}_3(\text{CO})_{11}]$.

Preparation of $\text{MHFe}_3(\text{CO})_{11}$ with $\text{M} = \text{Cs}$ or Rb . To an aqueous solution of $\text{NaHFe}_3(\text{CO})_{11}$ was added a slight excess of MCl . The brown microcrystalline product formed was collected, washed with water, and dried in vacuo to afford the pure material. Anal. Calcd for $\text{C}_{11}\text{HFe}_3\text{CsO}_{11}$: C, 21.67; H, 0.17. Found: C, 21.52; H, 0.20. Calcd for $\text{C}_{11}\text{HFe}_3\text{RbO}_{11}$: C, 23.50; H, 0.18. Found: C, 23.45; H, 0.11. The IR bands (ν_{CO}) in acetonitrile and the chemical shift of the hydride also appear at the same values as those of $(\text{HNEt}_3)[\text{HFe}_3(\text{CO})_{11}]$.

Results and Discussion

Interactions between the Bridging Carbonyl of $\text{HFe}_3(\text{CO})_{11}^-$ and Its Countercations in Solution. As shown in Table I, the stretching frequency of the bridging carbonyl group in the $\text{HFe}_3(\text{CO})_{11}^-$ anion varies with its countercation and the solvent used. In ether or dioxane, this frequency gradually increases on going from Li^+ to Cs^+ while, in acetonitrile, Me_2SO , or diglyme, all the $\text{MHFe}_3(\text{CO})_{11}$ salts exhibit the same ν value of bridging CO for the same solvent. More interestingly, two IR absorption bands (Figure 1b) were observed in THF in the bridging carbonyl region for each alkali metal salt $\text{MHFe}_3(\text{CO})_{11}$ with the high-frequency absorption occurring at 1745 cm^{-1} , independent of the countercation M^+ , and the low-frequency peak appearing in the range 1672–1700 cm^{-1} , varying with the cation. When an excess of HMPA, acetonitrile, or Me_2SO was allowed to add to the ether solution of $\text{KHFe}_3(\text{CO})_{11}$, the IR absorption band at 1679 cm^{-1} was shifted to a higher frequency at ca. 1730 cm^{-1} depending slightly on the ratio of ether to the added solvent (vide infra). The above observations along with the results from previous ion-pairing studies^{13,14} lead us to the following conclusions: (i) in ether, all the $\text{MHFe}_3(\text{CO})_{11}$ salts exist as contact ion pairs formed via the interaction between M^+ and the oxygen atom of the electron-rich bridging CO; (ii) both contact ion pairs and less associated forms are present in THF for all the alkali salts; (iii) only the less associated forms are present in CH_3CN , Me_2SO , diglyme, or CH_3NO_2 .

Further evidence supporting the presence of both contact ion pairs and less associated forms in THF was obtained from the titration of $\text{KHFe}_3(\text{CO})_{11}$ by dibenzo-18-crown-6. Successive addition of 1 equiv of dibenzo-18-crown-6 to the THF solution of $\text{KHFe}_3(\text{CO})_{11}$ results in a linear decrease in intensity of the low-frequency band at 1696 cm^{-1} corresponding to contact ion pairs and a concurrent linear increase in the absorbance of the 1745- cm^{-1} peak corresponding to the less associated forms (Figure 2). Similar techniques had been used to distinguish between contact ion pairs and less associated forms in other reports.¹¹⁻¹³

Careful examination of the bridging CO stretching frequencies of the contact ion pairs reveals that, for the same cation, the frequency decreases in the order $\text{THF} > \text{ether} > \text{dioxane}$, parallel to the donor ability of the solvent, while in the same solvent, the ν value of bridging CO increases in the

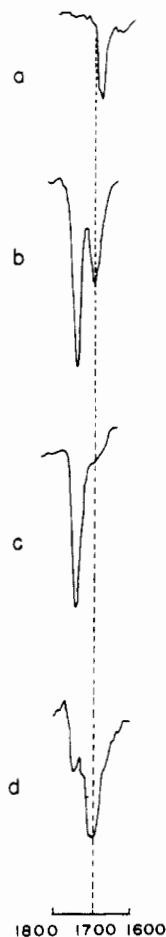
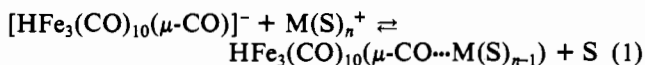


Figure 1. IR absorption bands of $\text{KHF}_3(\text{CO})_{11}$ in the bridging carbonyl region: (a) in ether; (b) in THF; (c) in a THF solution containing 1 equiv of dicyclohexyl-18-crown-6; (d) in ethanol.

order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+$, following the reverse order of Lewis acidity of the cation.¹⁵ The results can be understood in terms of a simple contact ion pair formation model (eq 1) in which the formation of a contact ion pair is



viewed as a replacement of one solvent molecule coordinated to the cation M^+ by the $\text{HF}_3(\text{CO})_{11}^-$ anion. The interactions of solvent molecules with the countercation exist both in the free cation and in the contact ion pair. According to the model, in the same solvent a lighter cation, a stronger Lewis acid than the heavier one, should give a stronger interaction with the bridging CO and consequently a lower ν value of bridging CO while, for the same cation M^+ , the attachment of stronger donor solvent molecules to the cation in the contact ion pair would result in a greater neutralization of the positive charge on the cation and lead to a higher ν value of the bridging CO. Thus, $\text{LiHF}_3(\text{CO})_{11}$ in dioxane, a system with the poorest donor solvent and the highest Lewis acidity cation compared to the other systems shown in Table I, has the lowest ν value of bridging CO at 1649 cm^{-1} . In ether or dioxane, the bridging CO of $\text{HF}_3(\text{CO})_{11}^-$ is a stronger competitor for the coordination sites on the countercation than the solvent molecule and only the contact ion pairs exist while, in THF, the donor ability of $\text{HF}_3(\text{CO})_{11}^-$ anion becomes comparable with that of the solvent and both contact ion pairs and the less associated forms are present. As the solvating power of the solvent further increases, the $\text{HF}_3(\text{CO})_{11}^-$ anion becomes less effective rel-

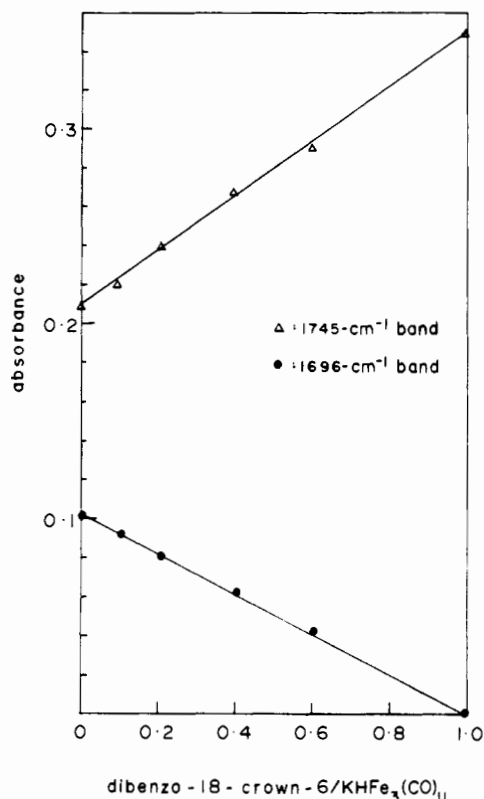


Figure 2. Titration of $\text{KHF}_3(\text{CO})_{11}$ in THF by dibenzo-18-crown-6.

Table II. Ratio of the Less Associated Forms to the Contact Ion Pairs of $\text{MHF}_3(\text{CO})_{11}$ in THF

alkali salt	less associated forms/ contact ion pair
$\text{LiHF}_3(\text{CO})_{11}$	~8
$\text{NaHF}_3(\text{CO})_{11}$	~6
$\text{KHF}_3(\text{CO})_{11}$	3.45 ± 0.13^a
$\text{RbHF}_3(\text{CO})_{11}$	2.12 ± 0.15^a
$\text{CsHF}_3(\text{CO})_{11}$	1.70 ± 0.07^a

^a Standard deviation.

ative to the solvent in the competition for the coordination sites on the cation M^+ and the equilibrium in eq 1 shifts far to the left. Therefore, only the less associated forms are observed by IR spectroscopy in CH_3CN , CH_3NO_2 , Me_2SO , or diglyme, which are known to have higher solvating power for the cation than THF.^{1,15}

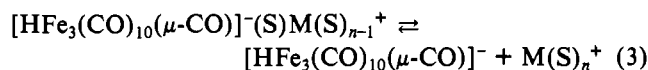
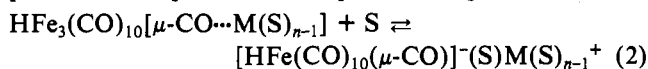
Ratio of Less Associated Forms to the Contact Ion Pairs in THF. The relative ratio of the less associated forms to the contact ion pairs in THF for each $\text{MHF}_3(\text{CO})_{11}$ can be estimated by the following method: the concentration of the less associated forms was calculated by using the corresponding PPN salt or $\text{K}^+\text{HF}_3(\text{CO})_{11}^-$ plus 1 equiv of dibenzo-18-crown-6 in THF as the standard, while the concentration of the contact ion pairs was obtained by subtracting the concentration of the less associated forms from the total concentration of $\text{MHF}_3(\text{CO})_{11}$. The results are given in Table II.

In contrast to the observations that the lighter cation interacts more strongly with the bridging CO group, the relative ratio as defined above decreases in the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$. Presumably, the driving force for this trend, which was also found in other ion-pairing studies,^{15,16} comes from the solvation energy of the cation, which decreases as the alkali metal cation goes from Li^+ to Cs^+ .

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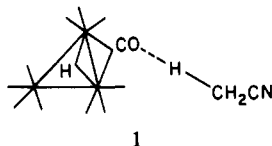
It is interesting to note that at concentrations between 10^{-1} and 10^{-2} M, the ratio of the less associated forms to contact ion pairs of $\text{KHF}_3(\text{CO})_{11}$, $\text{RbHF}_3(\text{CO})_{11}$, or $\text{CsHF}_3(\text{CO})_{11}$ is approximately a constant within the experimental error. For the analogous Li^+ and Na^+ salts, the contact ion pair concentrations are too small for an accurate IR measurement. The concentration independence of the relative ratio of the K^+ , Rb^+ , or Cs^+ salt strongly suggests that, in THF, the salt exists primarily as contact ion pairs and solvent-separated ion pairs, and an equilibrium as expressed in eq 2 is established.



If an appreciable amount of solvent-separated ion pairs further dissociates to free ions as shown in eq 3, a dependence of the ratio of less associated forms to contact ion pairs on the total concentration of $\text{MHFe}_3(\text{CO})_{11}$ should be observed.

Interactions between $\text{HFe}_3(\text{CO})_{11}^-$ and Solvents. It is noteworthy that for all the alkali metal salts $\text{MHFe}_3(\text{CO})_{11}$, existing as less associated forms, the bridging carbonyl stretching frequencies are independent of the cations but vary slightly with the solvents (Table I). For example, the bridging CO ν value of $\text{MHFe}_3(\text{CO})_{11}$ in acetonitrile is 1726 cm^{-1} for $\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+$ and the bridging CO ν values of $\text{HFe}_3(\text{CO})_{11}^-$ in THF, diglyme, acetonitrile, and CH_3NO_2 are 1745 (the less associated forms), 1740 , 1726 , and 1724 cm^{-1} , respectively. The independence of the bridging CO of the less associated forms on the countercation may be understood in view of the fact that the cation is no longer directly bound to the bridging CO, and hence it would not affect the ν value of the bridging CO.

In the less associated form, however, the anion $\text{HFe}_3(\text{CO})_{11}^-$ is now completely surrounded by the solvents and the solvent-anion interaction may become important. In fact, the slight dependence of the bridging CO stretching frequency with the solvent may be rationalized on the basis of the interaction, which is hydrogen bonding in nature (1), between the solvent

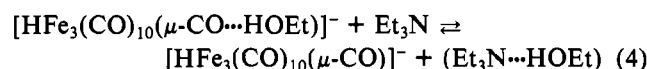


and the bridging CO. The more acidic the solvent, the stronger the interaction and the lower the CO stretching frequency. Thus, in CH_3CN or CH_3NO_2 where the protons are more acidic than those of THF or diglyme, the bridging CO ν value appears at $\sim 1725\text{ cm}^{-1}$, 20 cm^{-1} lower than the value of $\sim 1745\text{ cm}^{-1}$ in THF or diglyme.

The existence of hydrogen bonding between the bridging CO and the solvent is further demonstrated by the observations in alcohol solutions. Dissolution of $\text{MHFe}_3(\text{CO})_{11}$ in ethanol leads in all cases to two IR absorption bands at 1745 and 1699 cm^{-1} (Figure 1d) in the bridging CO region. Although two similar IR absorption bands at the bridging CO region were also observed in THF (Figure 1b), the behavior of the lower frequency bands in THF is different from the corresponding case in ethanol. In contrast to the results in THF that the frequency of the lower band changes with the cation used, the lower band in ethanol appears at the same frequency for all the metal cations M^+ . In addition, the observation that the intensity ratio of the 1745-cm^{-1} band to 1699-cm^{-1} band is independent of the cation in ethanol solution is also different from what was found for $\text{MHFe}_3(\text{CO})_{11}$ in THF (Table II). Apparently, the 1699-cm^{-1} band in ethanol does not arise from contact ion pairs, which should reveal dependence of the value

of ν_{CO} on the cation but more likely arises from the hydrogen bonding between the bridging CO and the hydroxyl group in ethanol. For convenience we would call this new species with its bridging CO absorption at 1699 cm^{-1} the "solvated form" to distinguish it from the contact ion pair and less associated form. The corresponding species of the higher frequency band at 1745 cm^{-1} , similar to the species of the 1746-cm^{-1} band in THF solution, are assigned as the less associated forms of $\text{HFe}_3(\text{CO})_{11}^-$, which do not interact with the hydroxyl group in ethanol. From Figure 1b,d it is clear that the solvated forms and less associated forms are in equilibrium in ethanol, while the contact ion pairs and the less associated forms coexist in THF. As shown by the IR spectrum, both solvated forms and less associated forms also coexist in methanol solution.

Further evidence in support of the existence of solvated forms was obtained when an excess of triethylamine was allowed to add to the ethanol solution of $\text{MHFe}_3(\text{CO})_{11}$. The addition results in a decrease in the absorbance of the 1699-cm^{-1} band with a concomitant increase in the intensity of the 1745-cm^{-1} band as expected from the viewpoint that hydrogen bonding is basically an acid-base reaction (eq 4).



The most convincing evidence in distinguishing the solvated forms from the contact ion pairs comes from the titration of $\text{KHF}_3(\text{CO})_{11}$ in ethanol by dibenzo-18-crown-6. In contrast to the behavior of $\text{MHFe}_3(\text{CO})_{11}$ in THF, the addition of the crown ether to $\text{KHF}_3(\text{CO})_{11}$ in ethanol does not influence the relative intensity of the two bands, further indicating that the 1699-cm^{-1} band is different in nature from that of the contact ion species.

It is noteworthy that only part of the $\text{HFe}_3(\text{CO})_{11}^-$ anions form hydrogen bonds with the ethanol molecules, while all of the anions exist as hydrogen-bonding species in CH_3CN , despite the fact that the hydrogen bonding in the former is much stronger than in the latter as shown by the ν_{CO} values.

In fact, similar results were found in the ion-pair studies of $\text{MHFe}_3(\text{CO})_{11}$ in THF. The lighter cation interacts more strongly with the bridging CO than the heavier one does, as denoted by the ν_{CO} in Table I, but the ratio of the less associated forms to the contact ion pairs of the lighter cation salt is higher than that of the heavier one. It thus appears that the strong interaction of the countercation with the bridging CO of $\text{HFe}_3(\text{CO})_{11}^-$ is also accompanied by an even stronger competition for the cation from the lone-pair electrons located on the oxygen atom in the THF molecule. Although the situation in alcohol or acetonitrile is not entirely the same, hydrogen bonds can also be formed either between solvent and $\text{HFe}_3(\text{CO})_{11}^-$ molecules or between solvent molecules themselves. It is the competition of these two forces that determines the ratio of solvated forms to the less associated forms. Apparently, $\text{HFe}_3(\text{CO})_{11}^-$ competes more effectively for the acidic proton on the solvent molecule in acetonitrile than in alcohol, so that all the $\text{HFe}_3(\text{CO})_{11}^-$ anions exist as solvated forms in acetonitrile, while both solvated and less associated forms are present in alcohol.

Another factor that can also affect the ratio of less associated forms to solvated forms is the ratio of the number of acidic protons to the number of pairs of nonbonding electrons in a solvent molecules. This ratio is $1/2$ in ethanol, while the value is 3 in acetonitrile. If intermolecular hydrogen bonding between the solvent molecules themselves requires an acidic proton and one pair of nonbonding electrons, two extra acidic protons in each acetonitrile molecule and one pair of nonbonding electrons in ethanol are left unbonded. The two acidic protons in acetonitrile can thus form hydrogen bonds readily with foreign molecules without competition similar to that in

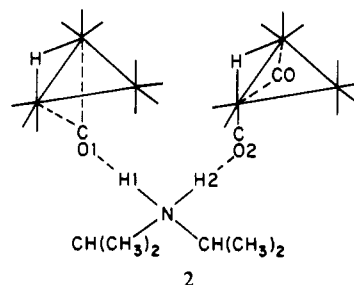
alcohol, and this might be the main reason that $\text{HFe}_3(\text{CO})_{11}^-$ is fully solvated in acetonitrile.

Interactions of Counteraction and $\text{HFe}_3(\text{CO})_{11}^-$ in the Solid State. Similar to the results observed in ether solution, the counteraction M^+ is also bound to the bridging CO in $\text{MHFe}_3(\text{CO})_{11}$ in the solid state as inferred from its relatively low bridging CO ν value compared to the ν value in acetonitrile (Table I). However, a noticeable difference in the trend of absorption frequency with the counteraction in the solid state and in solution was observed: the bridging CO ν value of the cesium salt at 1660 cm^{-1} is lower than the value of 1696 cm^{-1} for potassium and rubidium salts in the solid state, in contrast to the results in solution (Table I).

The IR absorption pattern of $\text{MHFe}_3(\text{CO})_{11}$ in solid state in the terminal carbonyl region is complicated and varies greatly with the counteraction, in contrast to the results observed in solutions. For the potassium and rubidium salts, a strong distinguished absorption occurs at 1906 cm^{-1} at the low end of the terminal CO region, which is absent for the corresponding cesium or PPN salt. The lowest terminal CO absorption of $\text{CsHFe}_3(\text{CO})_{11}$ occurs at 1930 cm^{-1} with a much weaker intensity than that of the 1906-cm^{-1} band described above. The higher bridging CO ν value and lower terminal CO ν value of $\text{KHFe}_3(\text{CO})_{11}$ and $\text{RbHFe}_3(\text{CO})_{11}$ relative to the cesium salt may be explained by the presence of a significant counteraction-terminal CO interaction, in addition to the known bonding between the cation and the bridging CO group in the potassium and rubidium salts. As a well-known phenomenon, the cation-terminal CO interaction would lead to an electron flow from the iron atoms to the π^* orbitals of the bonded t-CO group and a lower stretching frequency for the CO group. However, the interaction reduces the acidity of the cation, weakens the bonding between the cation and the bridging CO group, and consequently results in a higher bridging CO ν value for $\text{KHFe}_3(\text{CO})_{11}$ or $\text{RbHFe}_3(\text{CO})_{11}$ relative to that of $\text{CsHFe}_3(\text{CO})_{10}$, which lacks such a cation-terminal CO interaction.

Further evidence in support of the interaction comes from the similarity of the IR spectra of $\text{MHFe}_3(\text{CO})_{11}$ ($\text{M} = \text{K},$

Rb) and $[(i\text{-Pr})_2\text{NH}_2]^+[\text{HFe}_3(\text{CO})_{11}]^-$ and the structure of the latter compound. The $[(i\text{-Pr})_2\text{NH}_2]^+$ salt also exhibits a strong IR absorption band at 1880 cm^{-1} at the low end of the terminal carbonyl region, and the results of X-ray structure determination of the compound indicate that the two hydrogens in the $[(i\text{-Pr})_2\text{NH}_2]^+$ group interact with the bridging CO in one $\text{HFe}_3(\text{CO})_{11}^-$ and one terminal CO in the other $\text{HFe}_3(\text{CO})_{11}^-$ (2).¹⁷ This hydrogen bonding between the terminal CO



and the $[(i\text{-Pr})_2\text{NH}_2]^+$ group apparently accounts for the low CO stretching frequency at 1880 cm^{-1} . The close resemblance of the IR spectra of $\text{MHFe}_3(\text{CO})_{11}$ ($\text{M} = \text{K}, \text{Rb}$) to that of the $[(i\text{-Pr})_2\text{NH}_2]^+$ salt leads us to the conclusion that a similar, but weaker, cation-terminal CO interaction also exists in the two alkali salts.

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Registry No. $\text{KHFe}_3(\text{CO})_{11}$, 87145-35-5; $\text{LiHFe}_3(\text{CO})_{11}$, 87145-36-6; $\text{NaHFe}_3(\text{CO})_{11}$, 87145-37-7; $\text{CsHFe}_3(\text{CO})_{11}$, 38979-46-3; $\text{RbHFe}_3(\text{CO})_{11}$, 87155-47-3; $\text{Fe}(\text{CO})_5$, 13463-40-6; CO, 630-08-0; dibenzo-18-crown-6, 14187-32-7.

(17) Chen, C. K.; Cheng, C. H.; Hsu, C. S., results to be published. The bond distances are O1-H1 = 1.89 (1), O2-H2 = 2.09, N-O2 = 3.11, N-H1 = 1.078 (7), and N-H2 = 1.08 (1) Å. These values are in agreement with the formation of hydrogen bonds between O1 and H1 and between O2 and H2. See: Hamilton, W. C.; Ibers, J. C. "Hydrogen Bonding in Solids"; W. A. Benjamin: New York, 1968.

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Trans Chelation in Transition-Metal Complexes: Synthesis and Characterization of Palladium(II) Complexes of Bis(diphenylarsino)alkanes

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A number of synthetic routes to the bis(tertiary arsines) $\text{Ph}_2\text{As}(\text{CH}_2)_n\text{AsPh}_2$ ($n = 6-12, 16$) are described. These ligands form square-planar $\text{Pd}(\text{ligand})\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{CNS}$; $n = 6, 8, 10, 12, 16$) and $\text{Pd}(\text{ligand})\text{Cl}_2$ ($n = 7, 9, 11$) complexes, which have been characterized by elemental analyses, infrared and proton NMR spectroscopy, solid-state reflectance and solution visible/UV spectroscopy, and vapor-phase osmometry. Spectroscopic data indicate that the trans isomer is the only product when $n > 9$ and is the predominant one for $n < 9$. The molecular weights of the complexes are a function of the chelate chain length: polymeric species being preferred for short-chain ligands but monomeric units for the longer chain analogues ($n = 12, 16$). Evidence is given for the presence of both Pd-NCS and Pd-SCN linkages in the solid state and in solution for the thiocyanate derivatives. Factors affecting the formation of these trans-chelated complexes are discussed.

Introduction

The factors that govern trans chelation in square-planar transition-metal complexes have been a topic for much discussion in the recent literature,^{1,2} but no definitive postulate has yet appeared that explains the formation of cis and trans

bidentate chelate complexes. Since the isolation of the first trans-bonded bidentate complex by Issleib in 1961³ work on bidentate chelates with flexible backbones has indicated that the main factors that promote trans chelation are the presence

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