

Contribution from the Department of Chemistry,
Tulane University, New Orleans, Louisiana 70118**Solvent Effects on the Solution Structure and Chemical Properties of Lithium and Magnesium Salts of *trans*-Phenylacetyltricarbonyl(triphenylphosphine)iron(-I)**

M. YORK DARENSBOURG* and DRUSILLA BURNS

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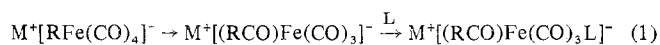
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The solution structure of *trans*-Ph₃PFe(CO)₃C(O)Ph⁻ as inferred from infrared spectroscopy varies with solvent and with cation. Direct evidence is presented for carbonyl oxygen-lithium cation interaction in diethyl ether whereas the ion pair is separated by adding small amounts of tetrahydrofuran or *N,N*-dimethylformamide. Stronger CO-M⁺ interaction is observed for M⁺ = MgCl⁺ in THF; this interaction may be interrupted by the addition of a solvent of higher dielectric constant such as DMF.

Introduction

Infrared spectroscopy is extremely useful for inferring the solution geometry of metal carbonyl complexes as well as for inferring specific interactions between metal carbonyl complexes and Lewis acids. For example Edgell, *et al.*, have made extensive use of ir spectroscopy to infer the solvent environment immediately surrounding the Co(CO)₄⁻ species.¹⁻³ Analysis of ν_{CO} indicated Na⁺Co(CO)₄⁻ to exist as a mixture of solvent-separated ions and associated ion pairs in tetrahydrofuran. Several other studies involving isolable organoaluminum adducts of transition metal carbonyls in which the R₃Al is bound to a bridging carbonyl oxygen atom have come from Shriver's laboratories.⁴

Only a few studies however have probed the importance of cation effect on chemical reactivity of transition metal carbonylate anions. In view of the observed rate dependence of the alkyl-acyl migratory insertion reaction described by eq 1,



(M⁺ = Li⁺ > Na⁺ ≫ (Ph₃P)₂N⁺), Collman has suggested that small polarizing cations stabilize negative charge developing on the acyl oxygen being formed during the course of the reaction.⁵

Our interest⁶ in L-L' exchange reactions of *trans*-LFe(CO)₃-C(O)R⁻ as well as the competition of alkylation reagents for various nucleophilic sites in such transition metal carbonylates prompted the following investigation of the ir spectra and chemical reactions of *trans*-Ph₃PFe(CO)₃C(O)Ph⁻ as a function of cation and solvent.

Experimental Section

All preparations and transfers were performed under N₂ or Ar atmosphere with rigorous exclusion of air.

Materials. Tetrahydrofuran was purified by reflux over and distillation under N₂ from the deep purple sodium benzophenone dianion immediately before use. Diethyl ether was distilled under N₂ from lithium aluminum hydride onto sodium. Phenyllithium and methylolithium were purchased from Alfa Inorganics and the Lithium Corp., respectively. Tri-*n*-butylphosphine and triphenylphosphine were the gifts of M & T Chemical Co. Benzylmagnesium chloride was

prepared by the usual Grignard procedure from triply distilled magnesium turnings donated by Dow Chemical Co.

Preparations and Reactions. Solutions of LFe(CO)₃C(O)R⁻M⁺ (M⁺ = Li⁺ or MgCl⁺) were prepared by syringing solutions of the appropriate RM reagent in near-stoichiometric amounts to solutions of LFe(CO)₄^{6,7} in rubber septum capped, degassed erlenmeyer flasks. In the solvent mixture studies LFe(CO)₃C(O)R⁻M⁺ compounds were prepared in 5.0 ml of the predominant solvent, THF or Et₂O, and small increments of the more basic solvent were added to this solution. Reactions were monitored using a Perkin-Elmer 521 infrared spectrophotometer as previously described.⁸

Results and Discussion

Metal carbonyl complexes of D_{3h} symmetry are expected to exhibit only one infrared-allowed band in the CO stretching region of the spectrum, an E mode.⁸ The splitting of the band centered at 1852 cm⁻¹ for Ph₃PFe(CO)₃C(O)Ph⁻Li⁺ in THF (species I) is consistent with the asymmetry of the acyl ligand. Such splitting of the E' mode is observed in spectra of *trans*-Ph₃PFe(CO)₃C(OEt)Ph in both polar and nonpolar solvents (Figure 1). In contrast, the analogous ν_{CO} region of the ir spectrum for Ph₃PFe(CO)₃C(O)Ph⁻Li⁺ in diethyl ether (species Ia) exhibits two well-separated bands, a somewhat asymmetric howbeit nonsplit band to slightly higher frequencies from the THF produced species I and a lower frequency band at 1810 cm⁻¹. Integrated infrared intensities show these bands to be in the ratio of 2:1 and this ratio is always maintained; *i.e.*, appearance or disappearance of one band is accompanied by the other. Table I contains ν_{CO} data for the compounds appropriate to this study.

Species I and Ia are produced by the dropwise addition of benzene-ether solution of PhLi in near-stoichiometric amounts to solutions of Ph₃PFe(CO)₄. By carefully monitoring the reaction of Ph₃PFe(CO)₄ in Et₂O with added PhLi solution it was noted that a spectrum similar to that of species I, *i.e.*, a single split band centered at 1850 cm⁻¹, was first produced; this changed into the spectrum of Ia with time (Figure 2).

Species I and Ia were found to be quantitatively interconvertible. Thus Ia could be produced by addition of PhLi to Ph₃PFe(CO)₄ in Et₂O or by production of I in THF, vacuum removal of THF, and addition of Et₂O to the residue. Sub-

(1) W. F. Edgell, M. Y. Yang, and N. Koizumi, *J. Amer. Chem. Soc.*, **87**, 2563 (1965).

(2) W. F. Edgell, J. Lyford, IV, A. Barbetta, and C. I. Jose, *J. Amer. Chem. Soc.*, **93**, 6403 (1971).

(3) W. F. Edgell and J. Lyford, IV, *J. Amer. Chem. Soc.*, **93**, 6407 (1971).

(4) For a recent review see D. F. Shriver, *Chem. Brit.*, 419 (1972), and references therein, specifically N. T. Nelson, N. E. Kime, and F. Shriver, *J. Amer. Chem. Soc.*, **91**, 5173 (1969).

(5) J. P. Collman, J. N. Cawse, and J. I. Braumann, *J. Amer. Chem. Soc.*, **94**, 5905 (1972).

(6) M. Y. Darensbourg and H. L. Conder, *Inorg. Chem.*, **13**, 506 (1974).

(7) H. L. Conder and M. Y. Darensbourg, *J. Organometal. Chem.*, **67**, 93 (1974).

(8) Although trigonal-bipyramidal *trans*-LFe(CO)₃L' systems have no formal σ_h , it is appropriate to regard the planar Fe(CO)₃ group as belonging to the symmetry group D_{3h}. That is, the two-band (equal intensity) ir pattern observed is due to a perturbation of the ir-active E' mode as the system goes toward C_s symmetry (E' transforms into A' + A'', of equal intensity). This is to be distinguished from the appearance of the expected two-band pattern of A₁ and E (intensity ratio of 1:2) that would be anticipated under C_{3v} symmetry.

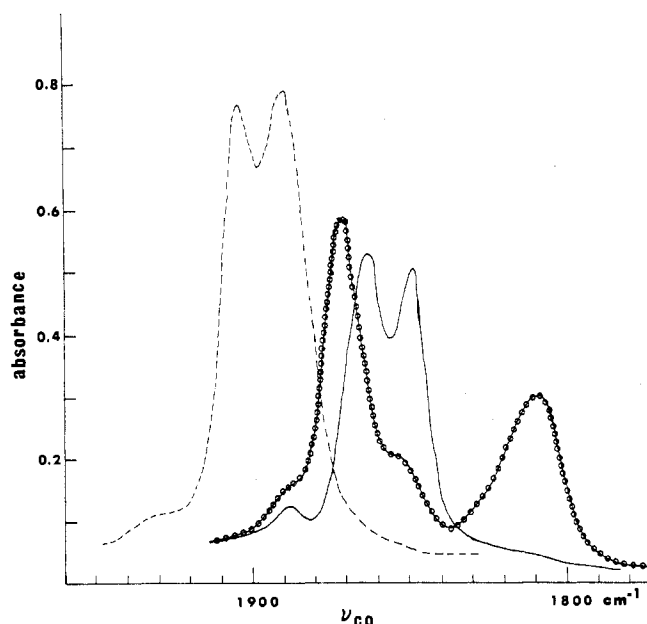


Figure 1. Infrared spectra of Ph₃PFe(CO)₃C(O)Ph⁻Li⁺ in THF (—) and Et₂O (---) and of trans-Ph₃PFe(CO)₃C(OEt)Ph in THF (---); 0.1-mm NaCl cells, ν_{CO} region.

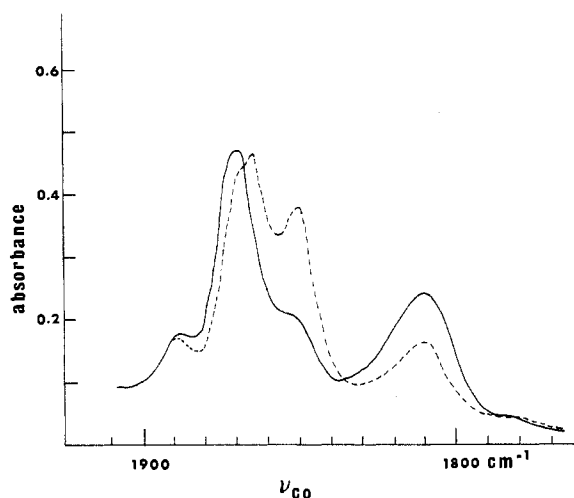


Figure 2. The reaction of 0.1 mmol of Ph₃PFe(CO)₄ with 0.1 mmol of PhLi in 5 ml of Et₂O at 25°: ---, 10 min; —, 20 min.

Table I. Carbonyl Stretching Frequencies of trans-LFe(CO)₃L'

L	L'	Solvent	ν _{CO} , cm ⁻¹
PPh ₃	C(OEt)Ph	Hexane	1912, 1899 (split E mode)
		THF	1905, 1893 (split E mode)
PPh ₃	C(O)Ph ⁻ Li ⁺	THF	1858, 1846 (species I) (split E mode)
		Et ₂ O	1871 s, 1808 m (species Ia)
PPh ₃	C(O)Me ⁻ Li ⁺	CH ₂ Cl ₂	1865 s, 1799 m
		THF	1848 br
PPh ₃	C(O)CH ₂ Ph ⁻ Li ⁺	Et ₂ O	1851 s, 1795 m
		THF	1848 br
PPh ₃	C(O)CH ₂ Ph ⁻ MgCl ⁺	THF	1864 s, 1807 m
		THF-DMF ^a	1851 br
P(n-Bu) ₃	C(O)Ph ⁻ Li ⁺	THF	1846, 1836 (split E mode)
		Et ₂ O	1851 s, 1795 m

^a 1.7 ml of DMF, 5 ml of THF.

sequent removal of Et₂O and dissolution into THF without exposure to air regenerated the spectrum of I.

Table II. Solvent Mixture Effects on Nature^a of Ph₃PFe(CO)₃C(O)Ph⁻Li⁺^b

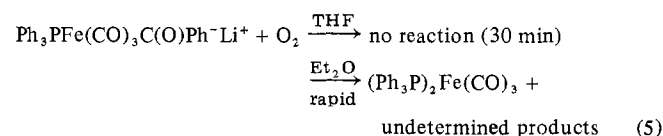
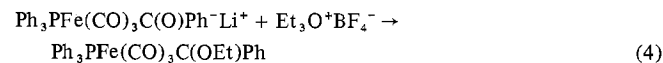
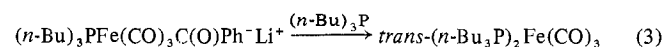
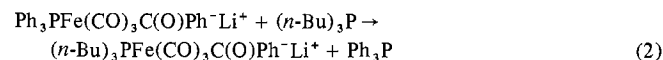
Solvent mixture	Mole ratio (solvent mixture)	Moles of complexing solvent/mol of Li ⁺	% species ^c	
			I	Ia
THF-Et ₂ O	5.10 × 10 ⁻³	7	10	90
	2.49 × 10 ⁻²	35	40	60
	3.70 × 10 ⁻²	52	60	40
	5.10 × 10 ⁻²	74	75	25
	7.35 × 10 ⁻²	109	90	10
DMF-Et ₂ O	>8.0 × 10 ⁻²	>115	100	0
	2.60 × 10 ⁻²	37	100 ^d	0

^a As indicated by ν_{CO} region of ir spectrum. ^b [Ph₃PFe(CO)₃C(O)Ph⁻Li⁺] = 7 × 10⁻³ M. ^c Species I is Ph₃PFe(CO)₃C(O)Ph⁻Li⁺ as observed in pure THF (split E mode at 1858, 1846 cm⁻¹); species Ia is Ph₃PFe(CO)₃C(O)Ph⁻Li⁺ as observed in pure Et₂O (two bands, 1871 (s) and 1808 (m) cm⁻¹). ^d The split band is at 1859, 1844 cm⁻¹.

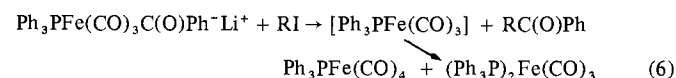
Both species I and Ia may exist simultaneously in appropriate solvent mixtures. As indicated in Table II, approximately 115 times as much THF as lithium salt is required to stabilize species I in Et₂O solution. This corresponds to 0.31 ml of THF in 5 ml of Et₂O. In contrast much less of the more polar *N,N*-dimethylformamide is required to change the spectrum of Ia into that of I in predominantly Et₂O solution. At DMF:Li⁺ ratios of 37 or greater, corresponding to 0.10 ml of DMF in 5 ml of Et₂O, complete conversion of Ia into I is effected.

The product of the reaction of benzylmagnesium chloride and Ph₃PFe(CO)₄ exhibits a two-band spectrum (similar to species Ia) in THF (Table I). Upon adding 1.7 ml of DMF to a 5-ml THF solution of [Ph₃PFe(CO)₃C(O)Bz]⁻MgCl⁺ the low-frequency band disappears and one band, centered at 1851 cm⁻¹ and flattened at the apex, appears.

Chemical properties of Ph₃PFe(CO)₃C(O)Ph⁻Li⁺ thus far investigated include ligand exchange, acyl exchange, *O*-alkylation by Et₃O⁺BF₄⁻, and air sensitivity, eq 2-5, respectively.⁶



The synthetically interesting *C*-alkylation by alkyl halides (eq 6) is under investigation in other laboratories.⁹



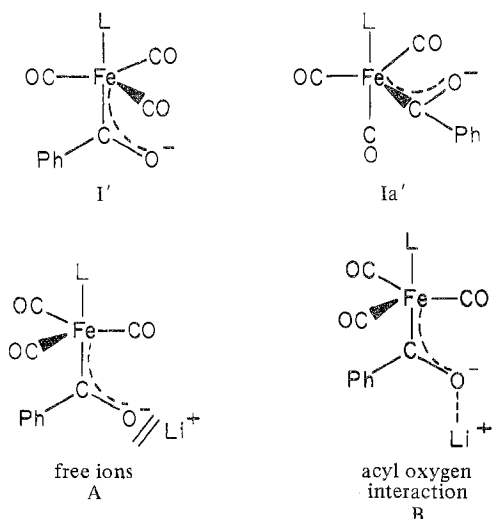
The course of reactions 2 and 3 is apparently the same in both THF and Et₂O. After a relatively rapid ligand-ligand displacement, acyl displacement proceeds much more slowly and the phosphine-disubstituted final product is obtained over a period of 3 days. The pseudo-first-order rate constant for the first step, indicated as (2), is 5 × 10⁻⁵ sec⁻¹ for THF solutions of [Ph₃PFe(CO)₃C(O)Ph⁻Li⁺] = 7 × 10⁻³ M and [(n-

$(n\text{-Bu})_3\text{P}] = 0.30\text{ M}$ at 70° .⁶ The rate of (2) is drastically affected by addition of more strongly Li^+ -coordinating agents such as hexamethylphosphoric triamide, HMPA. For example a 20:1 molar ratio of $\text{HMPA}:\text{Li}^+$ in THF solutions of I and $(n\text{-Bu})_3\text{P}$ produced a 10-fold increase in the rate constant of (2). Due to extreme overlap of product and reactant bands it was impossible quantitatively to follow the rate of (2) in Et_2O . Qualitatively however the rate of reaction 2 would appear to be the same in Et_2O as in THF if not more rapid in the former. That is, $(n\text{-Bu})_3\text{PFe}(\text{CO})_3\text{C}(\text{O})\text{Ph}^-\text{Li}^+$ (species IIa)¹⁰ is formed by the ligand-exchange process in Et_2O at 30° in a time period comparable to the analogous ligand-exchange process in THF at 70° . This suggests a different behavior of the ether-produced Ia species. It should be noted that carbene complexes of the type $\text{LFe}(\text{CO})_3\text{C}(\text{OEt})\text{R}$ readily undergo $\text{L}-\text{L}'$ exchange also obeying a first-order rate law (for the reaction $\text{Ph}_3\text{PFe}(\text{CO})_3\text{C}(\text{OEt})\text{Ph} + (n\text{-Bu})_3\text{P} \rightarrow (n\text{-Bu})_3\text{PFe}(\text{CO})_3\text{C}(\text{OEt})\text{Ph}$ in heptane at 72.9° , $k' = 1.1 \times 10^{-4}\text{ sec}^{-1}$; these reactions are somewhat slower in THF).¹¹

The iron acylates in THF may readily be converted into the carbene derivatives (eq 4) by treatment with $\text{Et}_3\text{O}^+\text{BF}_4^-$ *in situ*.⁶ This reaction is not facile in Et_2O . Removal of Et_2O from species Ia, dissolution into deaerated water, and addition of $\text{Et}_3\text{O}^+\text{BF}_4^-$ led to formation of *trans*- $\text{Ph}_3\text{PFe}(\text{CO})_3\text{C}(\text{OEt})\text{Ph}$, identical with the product resulting from ethylation of I in THF.

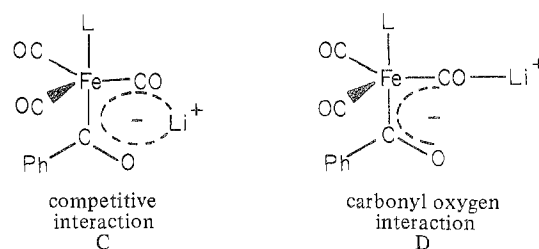
The air stabilities of I and Ia in solution vary drastically. Species Ia in Et_2O solution immediately decomposed upon being subjected to a 5-cm^3 portion of air. Similar behavior was not observed for I in THF; to the contrary, I may be handled in containers open to the atmosphere for short (30 min) periods of time. The air sensitivity of both Et_2O solutions and dried samples of Ia leads in both cases to the formation of *trans*- $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$.

The interconvertibility of I and Ia as well as the similarity of chemical properties such as the ligand-exchange reaction and formation of identical carbene derivatives for the two species suggests very similar structures. Possible structures might include the isomeric trigonal-bipyramidal forms (I' or Ia') or various formulations of ion pairs (A-D).



(10) The ir spectrum of IIa as prepared directly from the reaction of $(n\text{-Bu})_3\text{PFe}(\text{CO})_3$ and PhLi in Et_2O is identical with the ligand exchange product in Et_2O .

(11) D. J. Darensbourg and H. L. Conder, *Inorg. Chem.*, 13, 374 (1974).



The ν_{CO} spectrum of $\text{Fe}(\text{CO})_3(\text{diphos})$ in which the $\text{Ph}_2\text{-PCH}_2\text{CH}_2\text{PPh}_2$ is most likely bridging axial-equatorial coordination sites illustrates the complexity to be expected for such geometry (Figure 3).¹² The much different profile of the spectrum of Ia would tend to discredit the equatorial isomer possibility.

The theoretical system of a planar trigonally coordinated $\text{Fe}(\text{CO})_3$ with perturbation of one of the CO groups by O complexation with Li^+ has been analyzed in this laboratory.¹³ For such a system, illustrated in Figure 4, formal C_{2v} symmetry would allow the free CO groups two vibrational modes, an A_1 symmetric stretch and a B_1 asymmetric stretch. Due to the fact that in the symmetric stretch the interaction between CO vibrating groups is positive as opposed to being negative in the asymmetric stretch, the symmetric CO stretching vibration should occur at higher frequencies.¹⁴ Furthermore the perturbed CO (or O-complexed CO) has a vibrational mode also of A_1 symmetry. A much lower frequency is expected for this latter stretch since complexation effectively removes electron density from that CO. That is, the E (ir allowed) + A_1 (ir forbidden) mode of the unperturbed D_{3h} $\text{M}(\text{CO})_3$ transforms as $2A_1 + B_1$ in the species of lowered (C_{2v}) symmetry. All of these are ir active, thus predicting a three-band spectrum for ν_{CO} .

The above arguments may be used to analyze the spectrum of species Ia according to ion-pair formulations C or D and by assuming the A_1 and B_1 modes involving the uncomplexed CO's to be accidentally degenerate. As Figure 4 shows, coupling of the two A_1 modes will indeed move them closer in energy, possibly burying the high-frequency A_1 under the B_1 . Furthermore, the intensity ratio expected for a system such as the one described in the previous paragraph is 0.5:1.5:1.¹⁵ The observed intensity ratio of 2:1 is in keeping with our analysis of the high-frequency band being composed of two vibrational modes.

An effect on ν_{CO} very similar to that observed here has been observed by Kotz and Turnipseed in studies on the interaction of trimethylaluminum with the oxygen of a terminal CO ligand in (triphenylphosphonium cyclopentadienylidene)molybdenum tricarbonyl, $\eta^5\text{-(Ph}_3\text{PC}_5\text{H}_4\text{)Mo}(\text{CO})_3$.¹⁶ The 1:1 adduct exhibits two bands to slightly higher frequencies from those of the pure carbonyl complex and a third is

(12) W. R. Cullen and D. A. Harbourne, *Can. J. Chem.*, 47, 3371 (1969); W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, 8, 1464 (1969). Spectrum furnished by J. Tappan, this laboratory.

(13) D. J. Darensbourg, H. H. Nelson, III, and C. L. Hyde, *Inorg. Chem.*, 13, 2135 (1974).

(14) F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 84, 4432 (1962).

(15) The intensities of the three CO vibrational modes are related to the dipole moment change during the CO stretch (μ'_{MCO}) and α (half the angle between the two uncomplexed CO groups) assuming no coupling of the two A_1 vibrations in the following manner: $I_{B_1} = 2G_{tt} \sin^2 \alpha (\mu'_{\text{MCO}})^2$, $I_{A_1} = 2G_{tt} \cos^2 \alpha (\mu'_{\text{MCO}})^2$, and $I_{A_1}(\text{complexed}) = G_{tt}(\mu'_{\text{MCO}})^2$. Therefore, assuming all the μ'_{MCO} 's are approximately equivalent and $\alpha = 60^\circ$, $I_{A_1}:I_{B_1}:I_{A_1}(\text{complexed}) = 0.50:1.50:1.00$ or $(I_{A_1} + I_{B_1}):I_{A_1}(\text{complexed}) = 2:1$.

(16) T. C. Kotz and C. D. Turnipseed, *Chem. Commun.*, 41 (1970).

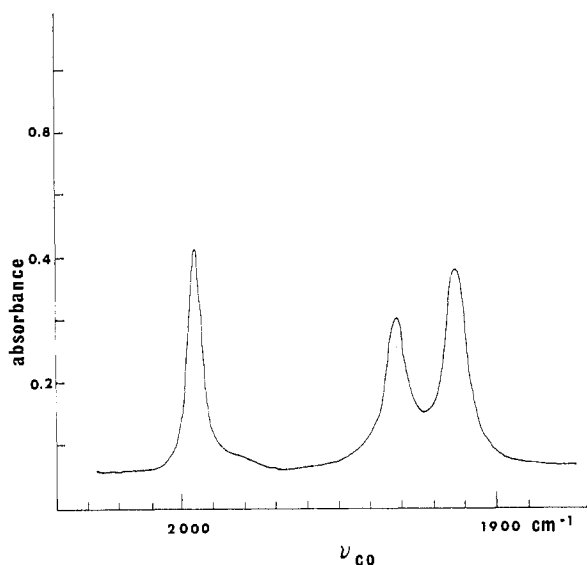


Figure 3. The infrared spectrum of (diphos)Fe(CO)₃ in the ν_{CO} region as example of the ir profile expected for an axial-equatorial substituted trigonal-bipyramidal system; ν_{CO} 1994 (s), 1929 (m), and 1910 (s) cm^{-1} in hexane solution, 1.0-mm NaCl cells.

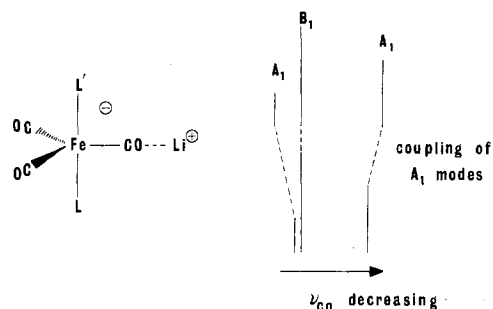


Figure 4. Analysis of trigonal Fe(CO)₃ with perturbation of one CO group by carbonyl oxygen-metal ion interaction.

developed at much lower frequencies, suggesting specific interaction with one carbonyl oxygen. Even more appropriate to this study, $[\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2\text{Mg}(\text{C}_5\text{H}_5\text{N})_4$ was shown by crystal structure analysis to contain a planar (py)₄Mg²⁺ with the two remaining octahedral sites occupied by one carbonyl oxygen of two adjacent $\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3^-$.¹⁷ Formation of the magnesium-oxygen bond is associated with a decrease of ca. 80 cm^{-1} in the lowest frequency carbonyl absorption and a slight increase in frequency of the two higher frequency bands. Such lowering of ν_{CO} upon coordination with a Lewis acid is also reported in the various studies by Shriver.⁴

(17) S. W. Ulmer, P. M. Skarstad, J. M. Burlitch, and R. E. Hughes, *J. Amer. Chem. Soc.*, **95**, 4469 (1973).

The position of the low-frequency band observed here, which according to our analysis is due to interaction of Li⁺ or MgCl⁺ with a specific CO group, is shifted by about -60 cm^{-1} from the uncomplexed CO groups. This shift is greater than that observed in studies of the solvent-dependent ion-pairing phenomenon of Na⁺Co(CO)₄^{-2,3}. Edgell, *et al.*, have observed a lowering of the T_d symmetry of Co(CO)₄⁻ in THF solutions of NaCo(CO)₄ (ν_{CO} 1886 (vs), 1858 (m) cm^{-1}), whereas small amounts of added water or DMF led to the simpler ir spectrum of the pure T_d species (ν_{CO} 1919 cm^{-1} in water, 1892 cm^{-1} in DMF). The appearance of the low-frequency band in THF of $\Delta\nu_{\text{CO}}$ -30 cm^{-1} was ascribed to the interaction of sodium ion in a monodentate fashion with a carbonyl oxygen of Co(CO)₄⁻. The larger $\Delta\nu_{\text{CO}}$ observed here would suggest a greater perturbation although certainly the interaction is not as great as those observed in adduct formation of terminal CO groups with organoaluminum compounds or Mg(py)₄²⁺. ($\Delta\nu_{\text{CO}}$'s are from -80 to -200 cm^{-1} for these cases.)

In summary, the work reported here offers direct evidence of carbonyl oxygen-cation interaction in iron carbonyl acylates. Species I, that is, LFe(CO)₃C(O)R⁻M⁺, produced in solutions which promote formation of free or solvent-separated ions is believed to exist as such (formulation A above), the acyl ligand exerting the same perturbing influence on the E mode of the trigonal Fe(CO)₃ center as the ethoxy-carbene ligand.¹⁸ The evidence suggests that, once formed, the LFe(CO)₃C(O)R⁻ anion provides a basic site for cation coordination other than or at least competing with the acyl oxygen. Thus on the basis of the great perturbation of a terminal CO group in solvents where ion pairing is promoted, ion-pair formulations C or D best describe species Ia although it is presently impossible to distinguish between the two possibilities.

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Registry No. trans-(PPh₃)Fe(CO)₃C(OEt)Ph, 42947-52-4; trans-(PPh₃)Fe(CO)₃C(O)Ph⁻Li⁺, 52571-02-5; trans-(PPh₃)Fe(CO)₃C(O)Me⁻Li⁺, 52571-03-6; trans-(PPh₃)Fe(CO)₃C(O)CH₂Ph⁻Li⁺, 52571-04-7; trans-(PPh₃)Fe(CO)₃C(O)CH₂Ph⁻MgCl⁺, 52571-06-9; trans-(PBu₃)Fe(CO)₃C(O)Ph⁻Li⁺, 52571-07-0.

(18) It should be noted however that formulation B is expected to give a similar ir pattern and in fact cannot be ruled out in the absence of conductivity studies. Such studies are under way in our laboratory.