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Conductivity Studies of Ion Pairing in Transition Metal Organics

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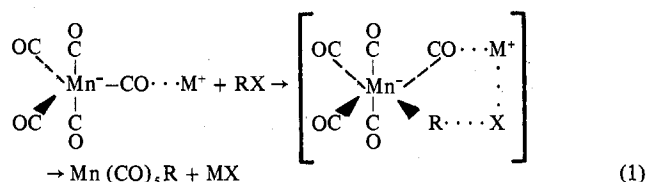
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The dependence of equivalent conductances on the concentration of THF solutions of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3^+\text{BPh}_4^-$, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{PMe}_2\text{Ph}^+\text{BPh}_4^-$, $(\text{Ph}_3\text{P})_2\text{N}^+\text{HFe}(\text{CO})_4^-$, $\text{Et}_4\text{N}^+(\mu\text{-H})[\text{Cr}(\text{CO})_5]_2^-$, and $\text{Li}^+\text{Mo}(\text{CO})_5\text{C}(\text{O})\text{Ph}^-$ and of CH_3CN solutions of $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{PMe}_2\text{Ph}^+\text{BPh}_4^-$, $(\eta^6\text{-C}_6\text{H}_6)\text{Mn}(\text{CO})_3^+\text{BPh}_4^-$, and $(\eta^6\text{-C}_6\text{H}_6)\text{Mn}(\text{CO})_3^+\text{ClO}_4^-$ were analyzed according to the Fuoss and Fuoss-Hsia equations. Ion-pair dissociation constants, K_D , of $\sim 10^{-5}$ were found for the cyclopentadienylmetal carbonyl salts in THF; the large cations Et_4N^+ and $(\text{Ph}_3\text{P})_2\text{N}^+$ were found to be as associated to metal carbonyl anions as were the alkali metal solvates, $\text{Li}(\text{THF})_x^+$ or $\text{Na}(\text{THF})_y^+$. A stronger ion pair was observed for the lithium acylate as indicated by a K_D on the order of 10^{-7} . Dissociation constants of approximately 10^{-3} determined for the cyclopentadienyl- and arenemetal carbonyls are among the smallest ever reported for salts in acetonitrile. Exact sites of ion interaction were not discernible in this study; however ion center-to-center distance parameters indicated that all of the salts studied in THF existed as contact ion pairs.

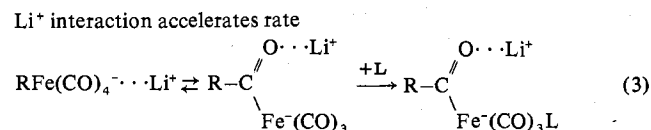
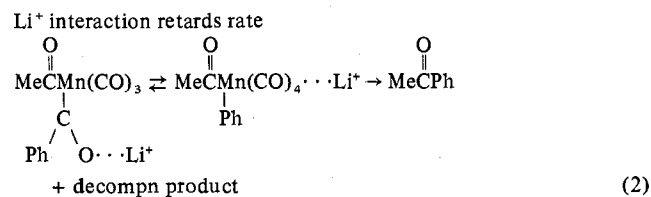
Introduction

The reactivity of organometallic salts may be quite dependent on ion-pairing effects as determined by contrasting reactions in solvents of different dielectric constants or by comparing reactivity with counterion variations. For example, the rate of reaction of $\text{M}^+\text{Mn}(\text{CO})_5^-$ with organic halides is inversely dependent on the dielectric constant of the solvent and also inversely dependent on the solution size of M^+ .¹ The temperature dependence of such reaction rates indicated that a larger negative entropy of activation was associated with the transition state containing an expanded coordination sphere still complexed to the larger or more solvated cation (eq 1).



A combination of conductance and infrared studies showed that considerable ion pairing existed for the carbonylate salts in Et_2O , THF, and THF-HMPA or THF-crown ether solvents.

In other examples, a preferential coordination of Li^+ to the benzoyl oxygen of *cis*-acetyl(benzoyl)tetracarbonylmanganese was suggested to be the cause of retardation of phenyl migration in the Li^+ salt as compared to the $\text{Ph}_3\text{PNPPH}_3^+$ salt (eq 2).² Also, in the somewhat opposite transformation



described by eq 3, small cations such as Na^+ or Li^+ were found to accelerate the rate of formation of a more basic acyl oxygen site from the more delocalized alkylcarbonyl anion.³

In another area, sites of nucleophilic attacks on arenemetal carbonyls have been observed to be solvent dependent. Methoxide ion attacked the ring of $(\eta^6\text{-C}_6\text{H}_6)\text{Mn}(\text{CO})_3^+$ to yield $(\eta^5\text{-C}_6\text{H}_6\text{OMe})\text{Mn}(\text{CO})_3$ in ether, while in methanol,

the carbonyl carbon was the site of reaction, producing $(\eta^6\text{-C}_6\text{H}_6)\text{Mn}(\text{CO})_2\text{CO}_2\text{Me}$.⁴

These and other observations indicate that a knowledge of solution environment about reactive centers is as vital to the understanding of organometallic salt chemistry as to that of carbanion and carbanion chemistry into which so much effort has been directed.⁵ Our present contribution to this problem is in the form of conductivity measurements on a series of π -arene- and cyclopentadienylmetal carbonyl complexes in which the metal carbonyl moiety is the cation, of the Li^+ salt of the acyl anion $\text{Mo}(\text{CO})_5\text{C}(\text{O})\text{Ph}^-$, of the $(\text{PPh}_3)_2\text{N}^+$ salt of a rather symmetrical anion, $\text{HFe}(\text{CO})_4^-$, and of the Et_4N^+ salt of $(\mu\text{-H})[\text{Cr}(\text{CO})_5]_2^-$.

Experimental Section

Materials. The salts $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{L}^+\text{BPh}_4^-$ ($\text{L} = \text{CO}$, PPh_3 , PMe_2Ph),⁶ $(\eta^6\text{-C}_6\text{H}_6)\text{Mn}(\text{CO})_3^+\text{BPh}_4^-$,⁷ $(\eta^6\text{-C}_6\text{H}_6)\text{Mn}(\text{CO})_3^+\text{ClO}_4^-$,⁷ $(\text{Ph}_3\text{P})_2\text{N}^+\text{HFe}(\text{CO})_4^-$,⁸ and $\text{Et}_4\text{N}^+(\mu\text{-H})[\text{Cr}(\text{CO})_5]_2^-$ ⁹ were prepared according to the literature cited. Repeated recrystallizations from appropriate solvents yielded compounds whose purity was checked by elemental analysis, melting points, and appropriate spectroscopic methods.

Solvents were distilled under N_2 from appropriate scavenging agents and used immediately. Tetrahydrofuran was distilled after refluxing over the purple sodium benzophenone dianion. The purification of acetonitrile suitable for conductance measurements involved an extensive process;¹⁰ it was predried over calcium hydride, fractionally distilled from phosphorus pentoxide, refluxed over CaH_2 , and fractionally distilled, very slowly, from the CaH_2 .

Conductance Measurements. The purity of solvents used in conductance studies was carefully monitored via resistance measurements. Acceptably pure THF had a specific conductance of $1.98 \times 10^{-8} \Omega^{-1} \text{cm}^{-1}$ or less; pure MeCN, $2.50 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ or less. Corrections for the conductance of the solvent were negligible at this purity level. The measured solvent conductances compare favorably with data obtained by others. Ashby et al. reported values of $4 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ and less for the specific conductance of pure THF.¹¹ Both lower and slightly higher values for the specific conductance of CH_3CN have been reported, for example, $(1-2) \times 10^{-7}$,^{12a} $(2-5) \times 10^{-8}$,^{12b} and $4.2 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$.^{12c}

All glassware used in the conductance studies, including that used in the distillation and collection of fresh solvent, was rinsed with ethanolic KOH and then with absolute ethanol (10 times) to remove trace adsorbed impurities. With the exception of the conductance cell itself, all glassware was flamed out under vacuum and thoroughly flushed with N_2 before use. The clean, dry conductance cell was fitted with a wired-on septum cap and flushed with N_2 for several minutes before use.

Stock solutions of the metal carbonyl salts were prepared by the accurate weighing of a sample and rapid transferral to a volumetric flask. Concentration in moles per liter was calculated from the weight of the salt. Lithium salts of the anions $\text{Mo}(\text{CO})_5\text{C}(\text{O})\text{C}_6\text{H}_5^-$ were

Table I. Measured Conductances

CpFe(CO) ₃ BPh ₄ ^a in THF		CpFe(CO) ₂ PMe ₂ - PhBPh ₄ in THF		CpFe(CO) ₂ PMe ₂ - PhBPh ₄ in CH ₃ CN	
10 ⁶ c ^b	Λ ^c	10 ⁶ c	Λ	10 ⁵ c	Λ
3.17	68.17	3.98	82.22	13.32	152.7
6.34	61.34	5.97	80.63	13.95	152.5
9.49	56.04	7.95	78.30	14.65	151.4
15.79	50.37	9.93	76.51	16.28	150.7
22.06	46.46	11.90	74.56	18.31	148.8
31.43	41.80	15.84	71.15	20.93	147.4
40.73	38.92	19.76	68.38	26.64	144.2
53.06	35.57	23.67	66.10	36.62	140.9
68.32	32.84	28.53	63.63	48.83	136.0
83.14	30.66	33.36	61.77	58.60	132.8
98.12	28.89	39.14	59.27	83.71	126.8
127.60	26.32	44.88	57.41	106.50	120.7
156.60	24.45	52.48	55.26	137.90	116.5
185.00	23.04	61.89	53.07	167.40	112.7
226.70	21.41	74.92	50.54	214.80	108.4
253.80	20.55	87.78	48.46		
293.50	19.52	104.10	46.24		
324.60	18.83				

^a Cp = η⁵-C₅H₅. ^b c is concentration in mol/l. ^c Λ is equivalent conductance in cm² Ω⁻¹ equiv⁻¹.

prepared by adding C₆H₅Li (Alfa Products, 1.8 M in 70:30 benzene-ether) to a THF solution of Mo(CO)₆.¹³ In order to form the acylate, it was necessary to exclude air scrupulously. Infrared spectra were recorded before and after the addition of C₆H₅Li; by using Beer's law plots of Mo(CO)₆, the concentration of the acylate stock solution was calculated from the difference between the initial and final Mo(CO)₆ absorbances.

The dependence of equivalent conductance on concentration was approached experimentally by both the concentration of an initially dilute solution and the dilution of an initially concentrated solution. In either case the N₂-flushed conductance cell was first rinsed with stock solution, until constant resistivity readings were obtained. The cell was then emptied of stock solution and rinsed with pure solvent repeatedly until high, constant resistivity readings were achieved. A measured volume of solvent or stock solution was then added to the dry, empty cell via syringe and resistivity readings were taken following the addition of successive aliquots of stock solution or solvent, according to the mode of concentration variation.

All studies were conducted at 22 °C. All machine calculations and graphical plots were done on the IBM 7044 at the Tulane University Computing Center.

Instrumentation. A Barnstead conductivity bridge, Model PM 70CB (range of 0.1–10⁻⁷ Ω, with reported maximum error of ±1 to ±3% within this range), was used to measure the resistivities of solutions. A Beckman Instruments Co. Model CEL-3A glass conductance cell with rigid, shiny platinum electrodes was calibrated using 0.1 demal aqueous KCl solution and the conductance data of Jones and Bradshaw.¹⁴ By this method, the cell constant was determined to be 0.238 cm⁻¹.

Table II. Derived Conductance Parameters^g

Cation ^a	Anion	Solvent	Anal- ysis by 10 ⁵ K _D eq no. (22 °C)	Λ ₀	λ ₀ ⁺	λ ₀ ⁻	r ₊ ^b	r ₋ ^b	r ₊ + r ₋	α	
CpFe(CO) ₃ ⁺	BPh ₄ ⁻	THF	4	1.63	79.2	39.3	40.3 ^c	4.53	4.41	8.94	6.7 ^d
CpFe(CO) ₂ PMe ₂ Ph ⁺	BPh ₄ ⁻	THF	4	4.35	91.7	51.4	40.3 ^c	3.47	4.41	7.88	7.7 ^d
		CH ₃ CN	5	332	155.3	97.6	57.7 ^c	2.45	4.13	6.58	12.1 ^e (2.7) ^e
		CH ₃ CN	4	365	155.3	97.5	57.7 ^c	2.44	4.13	6.57	
BzMn(CO) ₃ ⁺	BPh ₄ ⁻	CH ₃ CN	5	365	156.0	98.3	57.7 ^c	2.42	4.13	6.55	5.8 ^e
		CH ₃ CN	4	358	156.2	98.5	57.7 ^c	2.42	4.13	6.55	
BzMn(CO) ₃ ⁺	ClO ₄ ⁻	CH ₃ CN	4	272	205.3	101.8	103.4 ^c	2.34	2.30	4.64	
PPN ⁺	HF ₂ (CO) ₄ ⁻	THF	4	20	115						7.4 ^d
Et ₄ N ⁺	(μ-H)[Cr(CO) ₅] ₂ ⁻	THF	4	4.2	122						7.6 ^d
Na ⁺	Mn(CO) ₅ ⁻	THF	4	1.98 ^f	131	48.2 ^e	83	3.70	2.15	5.9	6.9 ^d
Li ⁺	Mn(CO) ₅ ⁻	THF	4	4.30 ^f	114	36.6 ^e	77	4.87	2.30	7.2	7.6 ^d
Na ⁺	Mn(CO) ₅ P(OPh) ₃ ⁻	THF	4	0.93 ^f	91	48.2 ^e	43	3.70	4.16	7.9	6.3 ^d
Li ⁺	Mo(CO) ₅ (O)Ph ⁻	THF	4	~0.01							

^a Cp = η⁵-C₅H₅; Bz = η⁶-C₆H₆; PPN⁺ = [(Ph₃P)₂N]⁺. ^b Stokes radii; eq 6. ^c Literature values; see text. ^d Electrostatic center-to-center distance from eq 7. ^e Contact ion center-to-center distance giving minimum in σΛ in eq 5 analysis.²² The physically absurd number is in parentheses. ^f Data from ref 1; measured at 26 °C. ^g Λ and λ values in cm² Ω⁻¹ equiv⁻¹; r values in Å.

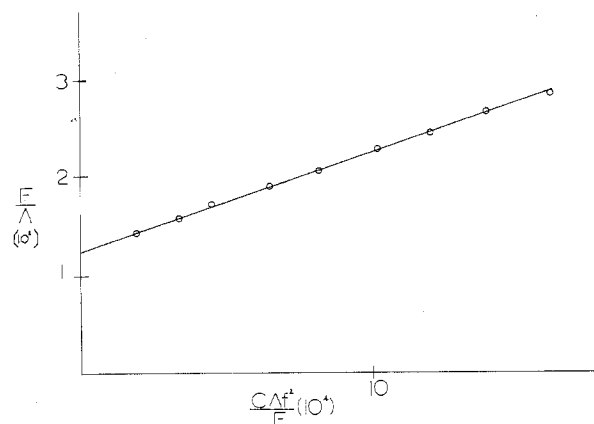


Figure 1. Conductance vs. concentration data treated according to Fuoss (eq 4) in the 10⁻⁴–10⁻⁶ M range for (η⁵-C₅H₅)Fe(CO)₃⁺BPh₄⁻ in tetrahydrofuran at 22 °C.

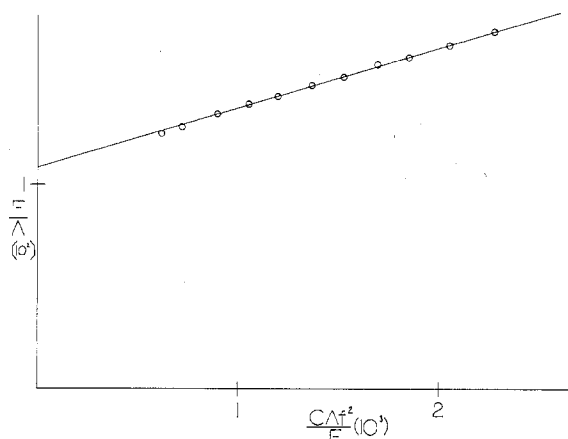


Figure 2. Fuoss plot for (η⁵-C₅H₅)Fe(CO)₂PMe₂Ph⁺BPh₄⁻ in THF.

Results

All electrolytes studied were found to be associated in both THF and CH₃CN solution. Sample conductance concentration data for several salts are listed in Table I. Concentration ranges studied were in general 10⁻⁴–10⁻⁶ M for THF solutions and 10⁻³–10⁻⁵ M for the acetonitrile studies. The upper value in both cases is below the critical concentration limit,¹⁵ defined by c₀ = 3.2 × 10⁻⁷D³, above which triple ions may exist. (For the much more associated acylate salt, aggregate formation is apparent at concentration greater than 10⁻⁵; hence the concentrations studied were from 10⁻⁶

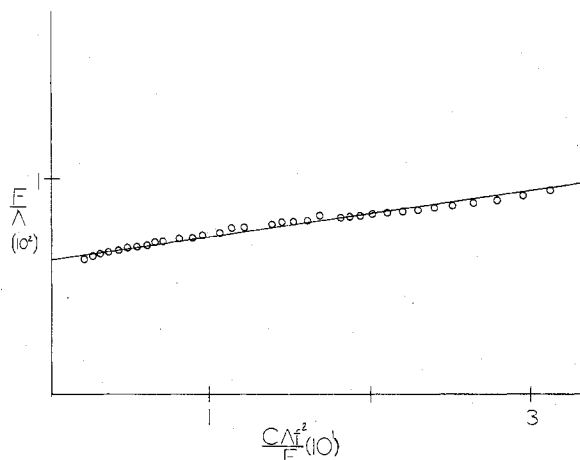


Figure 3. Fuoss plot in the 10^{-3} – 10^{-5} M range for $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{PMe}_2\text{Ph}^+\text{BPh}_4^-$ in CH_3CN .

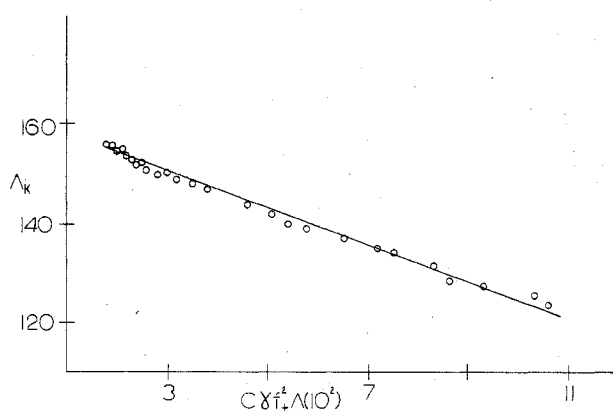


Figure 4. The same data as in Figure 3, treated according to the Fuoss-Hsia equation (eq 5).

to 10^{-5} M.) Examples of appropriate plots from which the conductance parameters, compiled in Table II, were derived are found in Figures 1–4. Figures 1 and 2 contain data collected in THF, dielectric constant $D = 7.39$,¹⁶ analyzed according to the Fuoss conductance equation, (4).^{1,15} Figure

$$F/\Lambda = 1/\Lambda_0 + c\Lambda f_{\pm}^2/\Lambda_0^2 FK_D \quad (4)$$

3 represents data collected in CH_3CN , $D = 35.99$,¹⁷ and also analyzed according to eq 4 whereas Figure 4 illustrates the same data treated according to the complete Fuoss-Hsia equation, rewritten in the linear form of eq 5.¹⁸ All symbols

$$\Lambda_K = \Lambda_0 - c\gamma f_{\pm}^2 \Lambda/K_D \quad (5)$$

in eq 4, 5, and 6, the Debye-Hückel activity coefficient for

$$-\ln f_{\pm} = e^2 \kappa / 2DkT (1 + \kappa a \gamma^{1/2}) \quad (6)$$

one-to-one electrolytes, have their usual meaning as discussed in ref 15.

Unlike those of our earlier study¹ the salts investigated here, with the exception of the acylates, were relatively air stable, and reproducible data were readily obtained utilizing the precautions described above. The uncertainty estimate in Λ_0 and K_D of $\pm 10\%$ ^{1,11} is felt to be a generous estimate for the arenemetal carbonyl salts and also appropriate for the Et_4N^+ and PPN^+ salts of metal carbonyl anions in this study.

The acylates however are very air sensitive, and furthermore the indirect concentration determination is subject to more error. On the other hand the dissociation constant value for $\text{Li}^+\text{Mo}(\text{CO})_5\text{C}(\text{O})\text{Ph}^-$, determined from the slope of the plot of F/Λ vs. $c\Lambda f^2/F$, is relatively insensitive to minor concen-

tration errors; K_D values of 1.04×10^{-7} , 8.89×10^{-8} , and 8.39×10^{-8} were obtained for calculated concentration:guess concentration ratios of 1, 1.25, and 0.75, respectively. Reproducible values of Λ_0 were not achieved; however, K_D values for several runs were consistently in the 10^{-7} range.

Single-ion limiting conductances were calculated according to Kohlrausch's law, $\Lambda_0 = \lambda_0^+ + \lambda_0^-$, using the following literature values in $\text{cm}^2 \Omega^{-1} \text{equiv}^{-1}$: in THF,¹⁹ $\lambda_0^-(\text{BPh}_4^-) = 40.3$, $\lambda_0^+(\text{Na}^+) = 48.2$, $\lambda_0^+(\text{Li}^+) = 36.6$; in CH_3CN ,^{12b} $\lambda_0^-(\text{BPh}_4^-) = 57.7$, $\lambda_0^-(\text{ClO}_4^-) = 103.4$. The hydrodynamic radii were calculated according to Stokes' law, eq 7. In

$$10^8 r_{\pm} = 0.819/\lambda_0^{\pm} \eta \quad (7)$$

addition, a center-to-center a value was computed for salts in THF solution according to the electrostatic expression, eq 8.²⁰

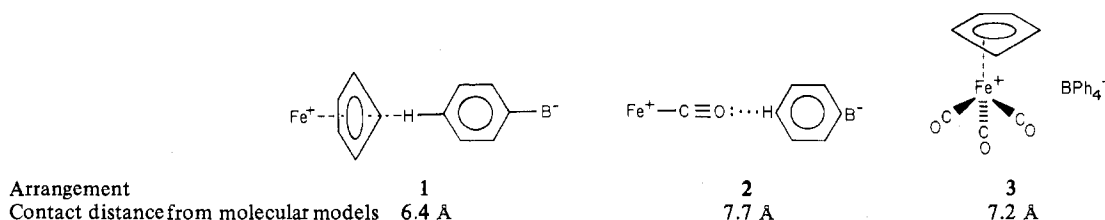
$$K_D = 3000/[4\pi N a^3 \exp(-e^2/aDkT)] \quad (8)$$

This electrostatic approximation does not hold for acetonitrile solutions; for such solvents of higher dielectric constants the Coulombic association described by (8) is relatively insensitive to ion size.²¹ The a values listed in Table II for CH_3CN solutions were those which gave a minimum standard deviation of fit of Λ_0 and K_D in eq 4, according to the method of Hanna et al.²² In this method, two minima in $\sigma\Lambda$, the standard deviation, have often been found.²³ When this was observed, both results are given. Because the magnitudes of K_D calculated according to eq 5 indicated that the arenemetal carbonyl salts were considerably associated in CH_3CN , the data were also submitted to analysis by eq 4 and are included in Table II for comparison.

Discussion

Ion-pair dissociation constant values on the order of 10^{-5} are observed for $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3^+\text{BPh}_4^-$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{PMe}_2\text{Ph}^+\text{BPh}_4^-$ in THF solution. These values are similar to those obtained for $\text{NaMn}(\text{CO})_5$ and derivatives previously investigated,¹ as well as to those obtained for simple inorganic salts such as M^+BPh_4^- ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Cs}$; $K_D \times 10^5 = 7.96, 8.52, 3.22, 0.187$, respectively).¹⁹ The much smaller K_D observed for $\text{Cs}^+\text{BPh}_4^-$ was attributed to a lack of solvation of the larger Cs^+ . The molecular volumes of the large cyclopentadienyl cations are more similar to that of the alkali metal ion plus a solvation sphere of four to six THF molecules than to that of unsolvated Cs^+ . Hence the K_D values of 1.64×10^{-5} and 4.35×10^{-5} observed here suggest very little solvation in the ion pairs.

Further evidence for little if any solvation of the cations is found in the electrostatic center-to-center distance, parameter a (eq 7). It is expected that the low charge density of the fairly symmetrical, large cyclopentadienyliron salts should allow for comparisons of contact distances derived from conductance data and those predicted from molecular structure data. Molecular model contact distances were calculated making use of the following crystallographic estimates: Fe–C, 1.86 Å;²⁴ C–O, 1.1 Å;²⁵ covalent radius of O, 0.7 Å; Fe–C₅H₅ ring plane, 1.7 Å;²⁶ covalent radius of C in an aromatic system, 0.7 Å;²⁴ effective crystallographic radius of BPh_4^- , 4.04 Å.^{12b} An average radius for the $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3^+$ ion was estimated at 3.2 Å, a value obtained by halving the ring C–Fe–carbonyl oxygen distance, computed by taking 2.05 Å as the Fe–C_{ring} distance.²⁶ The electrostatic center-to-center distance computed at 6.7 Å for $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3^+\text{BPh}_4^-$ is more readily correlated with arrangement 1, involving anion interaction with the ring, or with an average nonspecific interaction 3, than with 2. (The arrangement analogous to 2 is preferred for the metal carbonyl anion's interaction with the $x\text{THF}\cdot\text{Li}^+$ solvate, $\text{Li}^+\cdot x\text{THF}\cdots\text{OCMn}^-(\text{CO})_4$.)¹ The larger a value of the PMe_2Ph derivative reflects either ar-



arrangement 2 or the increased average radius of the phosphine-substituted cation in arrangement 3.

Thus specific points of cation-anion interaction are not readily defined in these studies; however it is certain that interstitial solvent molecules are not required to account for the center-to-center distances as derived from the electrostatic or K_D calculation. The Stokes radius, r_{\pm} , is an estimate of the size of an ion based on its solution mobility at concentrations approaching infinite dilution. The values of (r_+ + r_-) (and the corresponding Λ_0 and λ_0^+ values) of the cyclopentadienyl salts in THF apparently reflect some solvation of the smaller ($\eta^5\text{-C}_5\text{H}_5$) $\text{Fe}(\text{CO})_3^+$ ion "free" in solution, whereas the sums of hydrodynamic radii and the electrostatic center-to-center distance of the phosphine-substituted cation salt are practically the same.

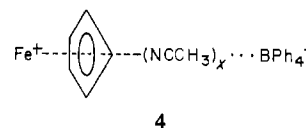
The K_D value of the phosphine-substituted cyclopentadienyliron compound is some 2.7 times larger than that of the tricarbonyl salt. Of the two effects which might account for this increase, increased size of the cation or decreased positive charge due to the substituent basic ligand, the latter argument is preferred in view of a previous observation. The dissociation constant of $\text{NaMn}(\text{CO})_4\text{P}(\text{OPh})_3$ is smaller than that of the all-carbonyl compound, $\text{NaMn}(\text{CO})_5$, by a factor of 2. That is, a substituent more basic than the CO ligand increases the negative charge dispersed onto the carbonyl oxygens (the point of cation interaction), enhancing ion-pair interaction compared to the all-carbonyl-containing ion when the carbonyl moiety is an anion. Likewise the substituent basic ligand on a cationic moiety decreases ion-pair interaction compared to the all-carbonyl cation.

Although reproducible data were not obtained for the $\text{Li}^+\text{Mo}(\text{CO})_5\text{C}(\text{O})\text{Ph}^-$ salts, it is clear that a much tighter ion pair exists in such compounds. Our unreported studies of $\text{Li}^+(\text{Ph}_3\text{P})\text{Fe}(\text{CO})_3\text{C}(\text{O})\text{Ph}^-$ similarly indicate very small K_D values and much aggregate formation at higher concentrations. These findings support the proposals of enhanced interaction of small cations with compounds containing acyl oxygens as opposed to more delocalized, all-carbonyl anions, which were based on chemical properties.^{2,3}

The dissociation constant values in CH_3CN solution are larger than those observed in THF by 100-fold; even so, the extent of association of these transition metal-organic salts in the more polar solvent is unusually high.²⁷ Yeager and Kratochvil²³ reported association constants ($K_A = 1/K_D$) of 4-60 for a series of alkali metal tetrafluoroborate, perchlorate, hexafluorophosphate, and tetraphenylborate salts. D'Aprano, Goffredi, and Triolo similarly reported K_A values of alkali metal and quaternary ammonium perchlorates in CH_3CN to range from 10 to 35 l./mol.²¹ The lower symmetry of the arene- and cyclopentadienylmetal carbonyl cations, as compared to the alkali metal and quaternary ammonium cations, presents sites of charge localization which may account for the increased association observed in this study. Consistent with this suggestion, the smallest previously reported K_D values determined in CH_3CN are for the chloride salt of the asymmetrical cation $[\text{Ph}_2(\text{NH}_2)\text{P}]_2\text{N}^+$ ($K_D = 3.2 \times 10^{-4}$)²⁸ and for salts of less symmetrical anions, NO_3^- and ClO_3^- ($K_D(\text{AgNO}_3) = 0.014$, $K_D(\text{LiClO}_3) = 0.0025$).^{29,30}

The r_+ values derived from limiting conductance values of ~ 100 for both ($\eta^5\text{-C}_5\text{H}_5$) $\text{Fe}(\text{CO})_2\text{PMe}_2\text{Ph}^+$ and ($\eta^6\text{-C}_6\text{H}_6$) $\text{Mn}(\text{CO})_3^+$ suggest no CH_3CN solvation of these cations in solution. Although the r_+ value of 2.45 Å for the former cation appears to be abnormally small, the agreement observed for the r_+ of ($\eta^6\text{-C}_6\text{H}_6$) $\text{Mn}(\text{CO})_3^+$ as determined from its BPh_4^- salt and from its ClO_4^- salt is quite good. The increase in the Stokes radius of ($\eta^5\text{-C}_5\text{H}_5$) $\text{Fe}(\text{CO})_2\text{PMe}_2\text{Ph}^+$ from CH_3CN to THF is in agreement with other results which indicate that CH_3CN , despite its higher dielectric constant, is a poorer solvating agent than is THF.¹⁹

Dissociation constants for simple alkali metal salts in CH_3CN computed according to eq 5 were found by Yeager and Kratochvil to be relatively insensitive to the a value used.²³ Furthermore the a values reported in that study, which used high-precision conductance measurements and the analysis performed here, do not appear to be highly reproducible. (Λ_0 and K_A values were for the most part identical in multiple studies of the same salt.²³) Hence the ion-pair contact distances reported in Table II for CH_3CN solution are to be interpreted at best with much caution. With this reservation, a rationale for the large difference in a for the ($\eta^5\text{-C}_5\text{H}_5$) $\text{Fe}(\text{CO})_2\text{PMe}_2\text{Ph}^+$ and ($\eta^6\text{-C}_6\text{H}_6$) $\text{Mn}(\text{CO})_3^+$ salts in CH_3CN that is based on preferred solvent interaction at the ring of both salts is proposed. Thus ion pairing through the face of the $\text{Mn}^+(\text{CO})_3$ moiety could give rise to the short contact distance computed. The large PMe_2Ph substituent of the cyclopentadienyliron derivative might then increase a by its bulk effect or promote a solvent-separated ion pair according to 4.

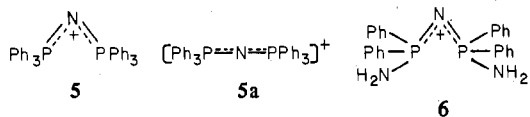


Alternatively, contact pairing of BPh_4^- through the slightly positive ring³¹ of the manganese cation gives a very reasonable model for the smaller a value.

The salts $\text{PPN}^+\text{HFe}(\text{CO})_4^-$ and $\text{Et}_4\text{N}^+(\mu\text{-H})[\text{Cr}(\text{CO})_5]_2^-$ are also extensively associated in tetrahydrofuran. The bis-(triphenylphosphine)iminium cation interacts somewhat less strongly with $\text{HFe}(\text{CO})_4^-$ than does the THF solvate of lithium, $\text{Li}\cdot x\text{THF}^+$, interact with $\text{Mn}(\text{CO})_5^-$. The interaction of tetraethylammonium and μ -hydrido-bis(pentacarbonylchromium(0)) is of about the same magnitude as the $\text{Li}(\text{THF})_x^+\text{Mn}(\text{CO})_5^-$ interaction. The sodium salt of $\text{Mn}(\text{CO})_5^-$ displays considerable contact ion pairing at higher concentration in THF as determined from the complexity of the CO ir pattern, whereas the simpler ν_{CO} infrared spectrum suggests the $\text{Mn}(\text{CO})_5^-$ to be in a symmetrical solvent environment in the lithium salt.¹ That is, the latter salt exists as solvent-separated ion pairs and these differences in solution structure are reflected in the K_D values determined by conductance measurements at lower concentrations. Hence with the relatively symmetrical carbonylates, THF-solvated cations and large unified cations would appear to play very similar roles with respect to ion pairing. Reactivity properties which depend on ion pairing such as entropies of activation,¹ protected sites, and counterion polarization of the reactive ion should also be similar.

There is however the problem of symmetry and charge distribution; for example, the symmetrical Et_4N^+ cation is

most likely structurally similar to the $\text{Li}(\text{THF})_x^+$ solvate. Structural parameters for the PPN^+ cation in a number of salts of metal carbonyl anions show a bent P-N-P angle in the range of $135\text{--}142^\circ$ (**5**);³²⁻³⁶ in the case of $\text{PPN}^+\text{V}(\text{CO})_6^-$



Bau and Wilson reported the first example of a linear P-N-P linkage (**5a**).³⁷ Both structures suggest considerable charge delocalization but for smaller, less solvated anions that charge is more available than in either symmetrical unified cations or in fully solvated cations. As example, the phosphonitrium cation, **6**, shows pronounced association as the chloride salt even in CH_3CN ($K_D = 3.2 \times 10^{-4}$ mol/l.).²⁸ The analogous SbCl_6^- derivative does not associate in CH_3CN , indicating that solvation of the cation predominates over anation of the much larger, symmetrical anion.

The utility of the PPN^+ ion toward stabilizing organometallic anions is well-known.³⁸⁻⁴¹ This has generally been ascribed to a crystal-packing effect with the implication being that the enhanced stability exists predominantly in solid forms of the salts. Our initial studies of the air sensitivity of $\text{HFe}(\text{CO})_4^-$ suggest that the stability enhancement upon substituting PPN^+ for Na^+ is effective both in the solid state and in THF or MeOH solution.⁴² One might rationalize this observation on the basis of either protection of the $\text{HFe}(\text{CO})_4^-$ by the large, associated PPN^+ cation or increased susceptibility to O_2 reaction due to polarization or distortion of $\text{HFe}(\text{CO})_4^-$ by contact ion-pair forms of $\text{Na}^+\text{HFe}(\text{CO})_4^-$. A dramatic example of counterion distortion in metal carbonyl anions was recently established in a crystal structure determination reported by Bau and Chin.⁴³ Whereas three of the C-Fe-C bond angles in $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 1.5(\text{dioxane})$ are tetrahedral, a fourth is distorted to 130° due to interaction with Na^+ .

The work presented here has shown that at the low concentrations used for conductivity measurements significant ion pairing occurs, even for salts of large cations and anions in a solvent of relatively high dielectric constant such as CH_3CN . Clearly intimate mechanisms proposed for reactions carried out in the concentration ranges generally used in reactivity studies (0.01-1 M) must include the possible effects of ion pairs and higher aggregates on the course of reaction. We have also given examples of asymmetric organometallic ions and commonly used cationic counterions whose charge localization or charge availability promotes ion-pair interaction. We are presently investigating chemical properties of transition metal ions which might depend on counterion structure as well as anion-cation interaction.

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Registry No. $\text{CpFe}(\text{CO})_3^+\text{BPh}_4^-$, 31781-41-6; $\text{CpFe}(\text{CO})_2\text{PMe}_2\text{Ph}^+\text{BPh}_4^-$, 32678-87-8; $\text{BzMn}(\text{CO})_3^+\text{BPh}_4^-$, 49564-34-3; $\text{BzMn}(\text{CO})_3^+\text{ClO}_4^-$, 49564-33-2; $\text{PPN}^+\text{HFe}(\text{CO})_4^-$, 56791-54-9; $\text{Et}_4\text{N}^+(\mu\text{-H})[\text{Cr}(\text{CO})_5]_2^-$, 16924-36-0; $\text{Na}^+\text{Mn}(\text{CO})_5^-$, 13859-41-1; $\text{Li}^+\text{Mn}(\text{CO})_5^-$, 15689-01-7; $\text{Na}^+\text{Mn}(\text{CO})_4\text{P}(\text{OPh})_3^-$, 59778-90-4;

$\text{Li}^+\text{Mo}(\text{CO})_5\text{C}(\text{O})\text{Ph}^-$, 60490-49-5.

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