and G. D. Shier, *J. Organomet. Chem.*, **21**, 495 (1970); (d) R. B. King and R. N. Kapoor, *Inorg. Chem.*, **8**, 2535 (1969); (e) C. O'Connor, *J. Inorg. Nucl. Chem.*, **32**, 2299 (1970); (f) J. K. Stille and R. W. Fries, *J. Am. Chem. Soc.*, **96**, 1514 (1974); (g) A. Sonoda, B. E. Mann, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 108 (1975); (h) E. C. Muetterties and F. J. Hirsekorn, *J. Am. Chem. Soc.*, **96**, 7920 (1974).

(7) K. J. Klabunde, *Acc. Chem. Res.*, **8**, 393 (1975).
(8) P. Fitton and J. E. McKeon, *J. Chem. Soc. D*, 370 (1969).
(9) R. F. Heck and J. P. Nolley, *J. Org. Chem.*, **37**, 2320 (1972).
(10) R. F. Hartley, "The Chemistry of Platinum and Palladium", Wiley, New York, N.Y., 1973.
(11) H. Gysling and M. Tsutsui, *Adv. Organomet. Chem.*, **9**, 361 (1970).

Oxidative-Addition Reactions of the $Na_2Fe(CO)_4$ Supernucleophile

James P. Collman,* Richard G. Finke, James N. Cawse, and John I. Brauman*

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305. *Received August 4, 1976*

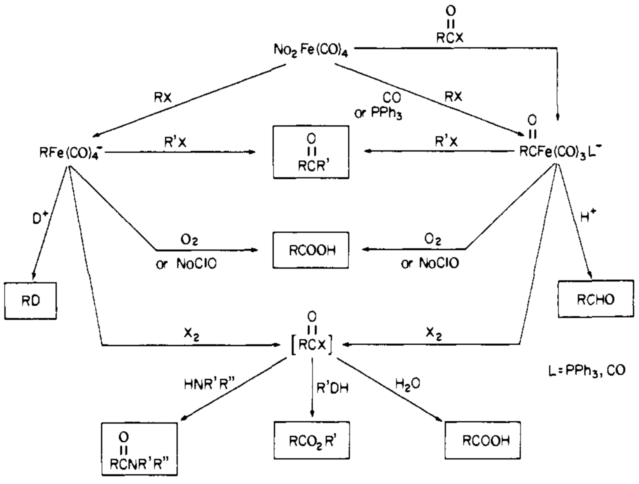
Abstract: A kinetic and mechanistic study of oxidative-addition of alkyl halides and tosylates to $Na_2Fe(CO)_4$ is presented which demonstrates a two-electron S_N2 oxidative-addition mechanism in both tetrahydrofuran (THF) and *N*-methylpyrrolidinone (NMP) with no detectable competing one-electron atom abstraction and/or radical chain mechanism. Evidence is presented delineating the importance of ion-pairing on the oxidative-addition reactions of transition metal anions. This study includes a wide variety of relative alkyl halide and tosylate substrate reactivities, activation parameters, the effect of added crown ethers, cryptands, and counterions (as $K_2Fe(CO)_4$), and salt effects. Also included are common-ion depression, stereochemical, conductivity, and crown ether or cryptand conductometric titration studies. The conductometric titrations using crown ethers or cryptands as titrants represent a new, simple, semiquantitative method for the determination of ion association constants. Data are presented which account for the dramatic 2×10^4 oxidative-addition rate increase in NMP vs. THF by the extent of dissociation of $Na_2Fe(CO)_4$, the more dissociated species being kinetically much more reactive. In NMP, $Na_2Fe(CO)_4$ dissociates predominantly to the solvent-separated supernucleophilic ion pair $[Na^+{:}S{:}Fe(CO)_4{}^{2-}]^-$ (S = solvent), the kinetically dominant species, with no kinetic contribution by free $Fe(CO)_4{}^{2-}$. In THF, $Na_2Fe(CO)_4$ is much less dissociated, with tight-ion paired $NaFe(CO)_4{}^-$ the kinetically important species. Values for the first and second Na^+ dissociation constants, in both THF and NMP, are presented. The results of recent x-ray studies of $Na_2Fe(CO)_4{\cdot}1.5$dioxane, $K_2Fe(CO)_4$, and $(\text{cryptate}{\cdot}Na^+)_2Fe(CO)_4{}^{2-}$ (cryptate = 4,7,13,16,21,24-hexaoxyl-1,10-diazabicyclo[8.8.8]hexacosane) are summarized and discussed.

The recent concept of oxidative-addition has enjoyed both a broad and unifying appeal in organotransition metal chemistry.[1] Mechanistic studies of oxidative-addition of alkyl halides[2] to d^7 transition metal compounds have resulted in the delineation of a one-electron atom abstraction mechanism of oxidative-addition.[3] Studies of d^8 complexes suggest a one-electron[1d,4] (atom abstraction and/or radical chain) in addition to a well-documented two-electron (S_N2)[5] oxidative-addition mechanism, depending upon the transition metal compound, the alkyl halide addendum, and the experimental conditions. These mechanisms have been the point of some controversy.[4,6] Oxidative-additions to d^{10} complexes are in general less well studied,[7] but recent work[1d,8] again suggests both one- and two-electron mechanisms for alkyl halide additions although these studies are also controversial.[8e] Detailed kinetic studies of d^{10} systems have appeared only for relatively reactive substrates such as CH_3I or $C_6H_5CH_2Br$.

Reactions employing initial oxidative-addition to $Na_2Fe(CO)_4$ were previously shown to be useful in the conversion of aliphatic halides and sulfonates into aldehydes,[9a] unsymmetrical ketones,[9b] carboxylic acids,[9c] esters,[9c] and amides[9c] (Scheme I). The use of $Na_2Fe(CO)_4$ in organic as well as inorganic synthesis has recently been reviewed.[10]

Previously we reported the dramatic effect of ion-pairing upon the alkyl migration reactions[11] of $[RFe(CO)_4]^-$ (Scheme I). Herein we report the characterization of $Na_2Fe(CO)_4$ as a supernucleophile,[5d] the importance of ion-pairing[12a] in the oxidative-addition reactions of this transition metal anion, elucidation of the extent of dissociation and kinetically dominant form of $Na_2Fe(CO)_4$ in both THF[13] and NMP,[13] and a full kinetic and mechanistic investigation of its oxidative-addition reactions.

Scheme I. Synthetic Organic Conversions Using $Na_2Fe(CO)_4$



Oxidative-addition of alkyl halides or sulfonates to $Na_2Fe(CO)_4$, d^{10}, coordinatively saturated iron(−II), yields a stable saturated d^8 alkyl iron(0) product (Scheme I), previously isolated and fully characterized as the air stable[13,14] salt $PPN^+[RFe(CO)_4]^-$. A recent x-ray diffraction study[15] of $PPN^+[CH_3CH_2CH_2Fe(CO)_4]^-$ shows a trigonal-bipyramidal structure (C_{3v} symmetry) with the alkyl group in the apical position, and an iron–carbon bond length of 2.20 (2) Å. The pattern of ν_{CO} frequencies in solution suggests that the C_{3v} symmetry is also maintained in solution,[14] although the single CO ^{13}C NMR signal[16] at ambient temperature of the CO's implies rapid scrambling of axial and equatorial groups, characteristic of many pentacoordinate complexes.[17] In the

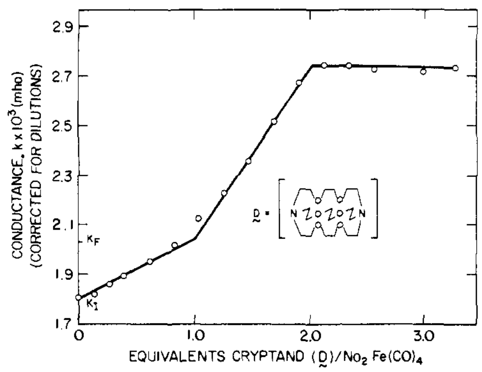


Figure 1. Conductometric titration of a 0.095 M $Na_2Fe(CO)_4$/NMP solution using the cryptand D.

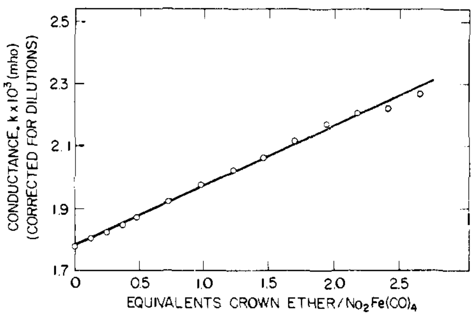


Figure 2. Conductometric titration of a 0.095 M $Na_2Fe(CO)_4$/NMP solution with dicyclohexyl-18-crown-6.

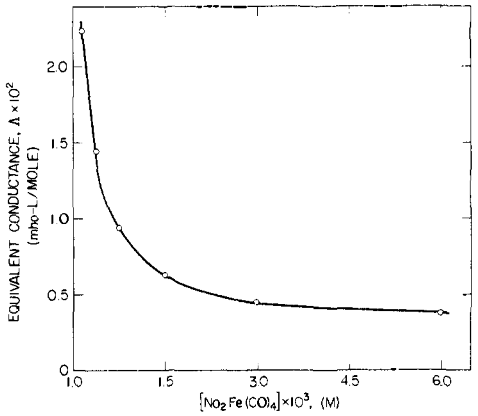


Figure 3. Equivalent conductance vs. $Na_2Fe(CO)_4$ concentration (THF, 25 ± 2 °C).

absence of air, THF solutions of $NaRFe(CO)_4$ are reasonably stable, decomposing[18] with a $t_{1/2} > 15$ h at 25.0 °C at an initial $NaRFe(CO)_4$ concentration of 0.016 M.

Initial observation of striking solvent effects, such as the (2×10^4)-fold increase in the rate of oxidative-addition of *n*-alkyl chlorides in NMP vs. THF led us to examine these reactions in detail.

Results and Discussion

Ion-Pairing in Solution. The Extent of Dissociation of $Na_2Fe(CO)_4$. Understanding the reactivity of $Na_2Fe(CO)_4$ in solution requires an understanding of its dissociation. Several species are possible in solution, ranging from ion-paired $Na_2Fe(CO)_4$ to totally dissociated $Fe(CO)_4{}^{2-}$ (Scheme II).

Scheme **II.** Dissociation of $Na_2Fe(CO)_4$

$$\underset{\text{A}}{Na_2Fe(CO)_4} \overset{K_{1D}}{\rightleftharpoons} Na^+ + \underset{\text{B}}{NaFe(CO)_4{}^-} \overset{K_{2D}}{\rightleftharpoons} 2Na^+ + \underset{\text{C}}{Fe(CO)_4{}^{2-}}$$

In addition, $Na_2Fe(CO)_4$ and $NaFe(CO)_4{}^-$ can exist as both tight (intimate) and solvent-separated (loose) ion-pairs.[20] Previous spectroscopic studies[21a,c] of $NaCo(CO)_4$ and $Na_2Cr_2(CO)_{10}$ have shown that these metal carbonyl anions form ion-pairs with alkali metal cations in solvents of low dielectric constant, and only a single report of the influence of ion-pairing upon their chemical reactivity has appeared.[21d] Naively, we might expect an increase in nucleophilicity C > B > A concomitant with the increasing degree of dissociation and increasing overall negative charge. For a solution of $Na_2Fe(CO)_4$ in the dipolar aprotic solvent NMP[13] freezing-point-depression studies indicate the predominant species is a uni-uni electrolyte. Naphthalene and the electrolytes sodium thiocyanate and DMDI[13] were found to have cryoscopic constants of 5.0 ± 0.3, 8.4 ± 0.5, and 15.0 ± 0.9 deg mol^{-1}, respectively, in NMP, consistent with their formulations as a nonelectrolyte, uni-uni electrolyte and di-uni electrolyte, respectively. The cryoscopic constant 8.8 ± 0.9 deg mol^{-1} found for 0.01-0.04 M $Na_2Fe(CO)_4$/NMP solutions shows that it is predominantly dissociated into $Na^+ + NaFe(CO)_4{}^-$ in NMP in this concentration range. More quantitative information on the values of K_{1D} and K_{2D}, Scheme I, was gained from the following simple experiment. A conductometric titration of $Na_2Fe(CO)_4$ in NMP using a cryptand,[22] Kryptofix 222,[23] as titrant shows two sharp break points (Figure 1). These break points occur at exactly 1 and 2 equiv of cryptand/$Na_2Fe(CO)_4$ corresponding, respectively, to the complete removal of 1, then 2 equiv of Na^+ from $Na_2Fe(CO)_4$ by the sodium complexing cryptand. (Kryptofix 222 has a Na^+ complexation constant of $\approx 10^8$ M^{-1} in MeOH.[24]) From the ratio of conductivities at the initial (no cryptand present) to the first equivalent point, K_{1D} is calculated[25a] to be $K_{1D} \simeq 0.28$ M. The data contained in this conductometric titration also prove[25b] that in NMP, $Na_2Fe(CO)_4$ does not form triple ions and that 2 or more equiv of cryptate form free $Fe(CO)_4{}^{2-}$. Furthermore, K_{2D} can be estimated[27] to be: 10^{-3} M > K_{2D} > 10^{-5} M. The failure of the crown ether, dicyclohexyl-18-crown-6, to produce even one clean break point in a similar conductometric titration (Figure 2) is consistent with these values.[28]

This simple method using a crown ether or cryptand conductometric titration for the determination of ion-dissociation constants for 1-1 electrolytes (i.e., K_{1D}) in strongly solvating media is much easier and as precise as any existing method.[33] In addition, this method also gives an estimate for K_{2D}.

In THF, $Na_2Fe(CO)_4$ is much less soluble than in NMP, its maximum solubility being $\sim 7 \times 10^{-3}$ M. The following experiments show $Na_2Fe(CO)_4$ is also much less dissociated in THF. The small magnitude of the conductance, 21.5 $\mu\Omega^{-1}$/cm at 0.006 M $Na_2Fe(CO)_4$, and the standard concave curvature of an equivalent conductance, Λ, vs. $Na_2Fe(CO)_4$ concentration plot (Figure 3) show that we are observing the first ion-pair equilibrium K_{1D} (Scheme II). This equivalent conductance (Λ) vs. concentration (*C*) data can be replotted using the Ostwald dilution law,[29a] eq 1, giving an order of magnitude estimate[30] of K_{1D} (THF) $\simeq 5 \times 10^{-6}$ M.

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_0} + \frac{\Lambda}{K_{1D}\Lambda_0{}^2} \qquad (1)$$

Unfortunately, the water sensitivity of $Na_2Fe(CO)_4$ and the fact that it is a 2-1 salt preclude the acquisition of more precise conductivity data, and its analysis using the Fuoss conductivity equation.[31] However, the value K_{1D} (THF) $\simeq 5 \times 10^{-6}$ M is consistent with the failure of the crown ether, dicyclohexyl-18-crown-6, to produce a break point in a conductometric ti-

Table I. Kinetic Data for Oxidative-Additions to $Na_2Fe(CO)_4$ in NMP:

$$Na_2Fe(CO)_4 + RX \xrightarrow[NMP]{25.0\ °C} Na^+[RFe(CO)_4]^- + NaX$$

Entry	$10^2[Na_2Fe(CO)_4]^a$ (M)	RX^b and $[RX] \times 10^3$ (M)		k_2 $(M^{-1}\ s^{-1})^c$	Miscellaneous exptl info
1	6.8		7.4	0.136	
2	6.8		3.7	0.146	
3	7.4		1.8	0.142	
4	3.3		3.7	0.159	
5	1.0		1.8	0.178	
6	3.2		36.9	0.154	
7	5.14		5.54	0.153	
8	11.0		7.39	0.131	
9	2.7		3.7	0.080	0.217 M $NaBPh_4$ added
		Bu_4NBPh_4 Salt Effect			
10	3.23		3.7	0.136	0.0773 M Bu_4NBPh_4
11	3.46		55.5	0.102	0.148 M Bu_4NBPh_4
12	2.46		55.5	0.052	0.215 M Bu_4NBPh_4
		Reactions with Different RX			
13	0.57	*n*-Hexyl chloride	2.71	5 ± 1^d	
14	8.5	*sec*-Octyl chloride	11.6	$k_2(\text{octane}) = 4.6 \times 10^{-3\,e}$ $k_2(\text{octenes}) = 3.3 \times 10^{-3}$	
15	4.3	Neopentyl bromide	3.95	0.117	
16	4.2	Neopentyl bromide	3.95	0.124	13% (0.0055 M) galvanoxyl added
17	0.753	Neopentyl bromide	3.95	0.34	0.025 M kryptofix 222[f] added
18	20.0	Neopentyl chloride	20.0	1.4×10^{-5}	
19	6.0	1-Adamantyl bromide	50.0	$<1 \times 10^{-5\,g}$	
20	$K_2Fe(CO)_4$, 4.18	Neopentyl bromide	3.95	0.0778	$K_2Fe(CO)_4$ used in place of $Na_2Fe(CO)_4$

[a] Effective $Na_2Fe(CO)_4$ concentration (see the experimental section). [b] RX = 2-ethylchlorobutane unless specified otherwise. [c] All data at 25.0 ± 0.1 °C. For all reactions (except numbers 6, 11, 12, 13, 17), $k_2 = k_1/[Na_2Fe(CO)_4]$ (effective), where k_1 is the average pseudo-first-order least-squares rate constant for the disappearance of reactants (measured after acid quench as RX) and appearance of products (measured after acid quench as RH). For entires numbers 6, 11, 12, 13, 17 done under second-order conditions, k_2 is the average second-order least-squares rate constant. Reactions pseudo-first-order with $Na_2Fe(CO)_4$ in excess gave log plots linear over at least three half-lives. Reactions run under second-order conditions gave linear plots over ~1.4 half-lives. [d] Standard deviation of four experiments. [e] k_2 for the disappearance of *sec*-octyl chloride = $7.9 \times 10^{-3}\ M^{-1}\ s^{-1}$. GLC product analysis shows 59% octane and 41% of a mixture of 1- and 2-octenes. [f] Kryptofix 222 is the trade name (E. M. Laboratories) for the cryptate 4,7,13,16,21,24-hexaoxy-1,10-diazabicyclo[8.8.8]hexacosane. [g] Monitored by IR.

tration in THF. In this solvent the Na^+ binding constants of the crown ether and $NaFe(CO)_4^-$ appear to be of comparable magnitude.[28] The stronger Na^+ complexing agent Kryptofix 222 cannot be used as a titrant due to the insolubility of $(\text{cryptate}{\cdot}Na^+)_2Fe(CO)_4^{2-}$.

From these conductivity, conductometric titration and freezing-point-depression studies we have shown that: (1) In THF (dielectric constant (ϵ) = 7.58 at 25 °C) $Na_2Fe(CO)_4$ exists predominantly as ion-paired $Na_2Fe(CO)_4$ in equilibrium with Na^+ and $NaFe(CO)_4^-$, $K_{1D} \simeq 5 \times 10^{-6}$ M and thus $K_{2D} \ll 5 \times 10^{-6}$ M. (2) In NMP, ($\epsilon = 31.5$ at 25 °C) $Na_2Fe(CO)_4$ is almost completely dissociated into Na^+ and $NaFe(CO)_4^-$, $K_{1D} \simeq 0.28$ M, with little dissociation to $Fe(CO)_4^{2-}$, 10^{-3} M $\geq K_{2D} \geq 10^{-5}$ M.

The large increase in the degree of dissociation of $Na_2Fe(CO)_4$ in NMP vs. THF is consistent with the well-known ability of dipolar aprotic solvents such as NMP to effect ion-pair dissociation by cation solvation.

Kinetic Studies of Oxidative-Additions to $Na_2Fe(CO)_4$ in NMP. Since $Na_2Fe(CO)_4$ is much more soluble in NMP than in THF (>0.2 M) and gives rapid and often quantitative oxidative-addition reactions for most alkyl halides, NMP is an ideal solvent for these kinetic studies. A compilation of kinetic results from oxidative-addition of various alkyl halides to $Na_2Fe(CO)_4$/NMP solutions is shown in Table I.

Table I shows that: (1) The oxidative-addition reactions are unusually facile, *n*-chlorohexane reacting with a half-life of under a minute (entry 13, Table I), and neopentyl bromide with a half-life of about 2 min (entry 15). (2) The reaction is apparently overall second-order, first-order in both alkyl chloride (entries 1-3) and $Na_2Fe(CO)_4$ (entries 3-8), but with a slight added dependence upon $[Na_2Fe(CO)_4]$, k_2 (observed) *increasing* from 0.131 to 0.178 $M^{-1}\ s^{-1}$ as $[Na_2Fe(CO)_4]$ *decreases* from 0.11 to 0.01 M. (3) Added $NaBPh_4$ (8 equiv of $NaBPh_4/Na_2Fe(CO)_4$) slows the reaction 49% (entry 9). (4) Added Bu_4NBPh_4 also slows the reaction (entries 10, 11) 8.7 equiv of $Bu_4NBPh_4/Na_2Fe(CO)_4$ giving a threefold decrease in k_2 (entry 12). (5) The reaction rate decreases in the order primary > $(CH_3CH_2)_2CHCH_2$- > secondary > neopentyl with no observable reaction in 9 days using 1-bromoadamantane (entries 13, 1, 14, 18, 19, respectively). (6) The reaction rate for neopentyl bromide is increased 2.8-fold by added cryptand[23] (2.5 equiv/$Na_2Fe(CO)_4$) (entry 17), is unaffected by the free-radical scavenger galvanoxyl (entry 16) and is decreased only 35% when $K_2Fe(CO)_4$ is used in place of $Na_2Fe(CO)_4$.

These results can be quantitatively accommodated by the following mechanism (Scheme III), which is also supported by additional evidence (vide infra). Solvent-separated ion-paired $(Na^+{:}S{:})_2Fe(CO)_4^{2-}$ is in a dissociative equilibrium with Na^+ and solvent-separated ion-paired $(Na^+{:}S{:}Fe(CO)_4^{2-})^-$. Both $(Na^+{:}S{:})_2Fe(CO)_4^{2-}$ and $(Na^+{:}S{:}Fe(CO)_4^{2-})^-$ can undergo S_N2 type oxidative-additions with different rate constants $k_{2\pm}$ and k_{2-}, respectively. The interesting increase in k_2(obsd) as the $Na_2Fe(CO)_4$ concentration decreases (Figure 4) arises from the nonlinear concentration dependence[12a] of $[Na^+{:}S{:}Fe(CO)_4^{2-}]^-$ via the dissociative equilibrium (K_{1D}, Scheme III). As the concentration of Na_2Fe-

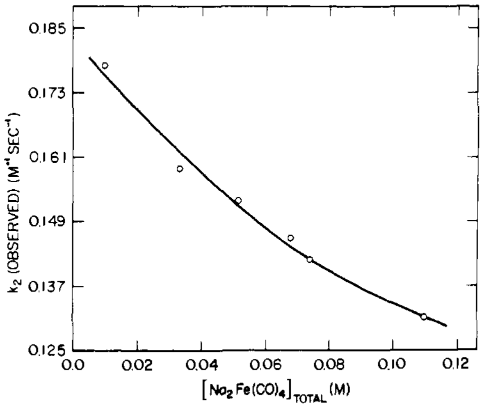
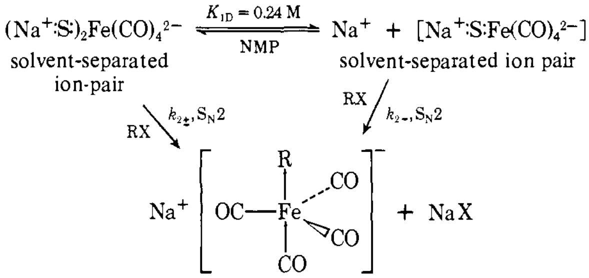


Figure 4. Dependence of k_2(obsd) upon $[Na_2Fe(CO)_4]$ for: $Na_2Fe(CO)_4$ + $(CH_3CH_2)_2$ $CHCH_2Cl$ → $Na^+[(CH_3CH_2)_2CHCH_2Fe(CO)_4]^-$ + NaCl (25.0 °C in NMP). The circles are experimental points and the line is from a second-order polynomial least-squares fit.

$(CO)_4$ decreases, the degree of dissociation, α, increases, and if $k_{2-} > k_{2\pm}$, k_2(obsd) increases (eq 5, Scheme III). Modeling[32] the k_2(obsd) vs. $Na_2Fe(CO)_4$ concentration data using the mechanism presented in Scheme III yields a value of $K_{ID} = 0.24 \pm 0.04$ M, in excellent agreement with the value $K_{ID} \simeq 0.28$ M determined by the conductometric titration, and the important result that $k_{2-} > 3k_{2\pm}$ with $k_{2-} = 0.184 \pm 0.003$. The value $K_{ID} = 0.24 \pm 0.04$ M is also a nontrivial finding. Even the imprecise determination of ion dissociation constants in strongly solvating media such as NMP is a difficult task.[33]

Scheme III. Mechanism of Oxidative-Addition to $Na_2Fe(CO)_4$ in NMP



From Appendix I (in NMP):

$$\frac{d[NaRFe(CO)_4]}{dt} = k_2(\text{obsd})[Na_2Fe(CO)_4]_{\text{total}}[RX] \quad (4)$$

where

$$k_2(\text{obsd}) = (k_{2-} - k_{2\pm})\alpha + k_{2\pm} \quad (5)$$

For a large K_{ID}:

$$k_2(\text{obsd}) \simeq -(k_{2-} - k_{2\pm})\frac{[Na_2Fe(CO)_4]_{\text{total}}}{K_{ID}} + k_{2-} \quad (9)$$

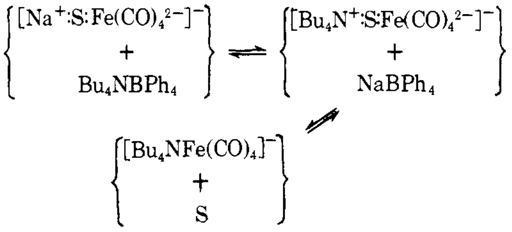
The small, 49%, common-ion rate depression observed in NMP for an eightfold excess of $NaBPh_4$ over $Na_2Fe(CO)_4$ requires that free $Fe(CO)_4^{2-}$ is not kinetically important—even in NMP.[34] This common-ion rate depression study also supports the values $K_{ID} = 0.24$ M and $k_{2-} > k_{2\pm}$. The expected Na^+ depression using the mechanism of Scheme III with $K_{ID} = 0.24$ M and $k_{2-} \ll k_{2\pm}$ (i.e., $k_{2\pm} = 0$) is 56%, in good agreement with the observed 49% decrease. If $k_{2\pm} = (1/8)k_{2-}$, the 49% decrease can be fit exactly.

The kinetic studies in NMP further support a S_N2 mechanism of oxidative-addition. The overall second-order rate law when ion-pairing is accounted for, the fact that $k_{2-} \geq 3k_{2\pm}$, and the alkyl halide substrate reactivities; primary > $(CH_3CH_2)_2CHCH_2$- > secondary > neopentyl ≫ adamantyl, resemble classic S_N2 reactions. The fact that adamantyl bromide is unreactive, $k_2 < 1 \times 10^{-5}$ M^{-1} s^{-1}, argues against a facile electron-transfer/halogen-abstraction component in these reactions. Although both d^{10} and d^8 systems show free-radical chain behavior[4,8] for oxidative-addition of poor S_N2 substrates (i.e., neopentyl bromide) as well as an apparent S_N2 mechanism for good S_N2 substrates (i.e., CH_3I), in the present case, we can find no evidence for a radical chain mechanism. Even for neopentyl bromide, oxidative-addition to $Na_2Fe(CO)_4$ is uninhibited by 13 mol % of the free radical scavenger galvanoxyl. The quantitative yields of a single product RH (after acid quench of $NaRFe(CO)_4$), the lack of radical coupling products such as R-R, the clean reproducible second-order kinetics observed, and the lack of inhibition by free radical scavengers strongly argue against the presence of a free-radical chain mechanism even when poor S_N2 substrates are used.

Our results in NMP further suggest that the predominant species present in $Na_2Fe(CO)_4$/NMP solutions is solvent-separated $[Na^+:S:Fe(CO)_4^{2-}]^-$. The oxidative-additions in NMP are counterion insensitive. The small, 2.8-fold rate increase observed when 2.5 equiv of Kryptofix 222/$NaFe(CO)_4$ are added, and the small, 35% rate decrease when $K_2Fe(CO)_4$ is used in place of $Na_2Fe(CO)_4$ are consistent with solvent-separated $[Na^+:S:Fe(CO)_4^{2-}]^-$ being the major species present in NMP solutions. If the predominant species in NMP were tight ion-paired $[MFe(CO)_4]^-$ (M = Na^+, K^+), the oxidative-additions would certainly be more counterion sensitive. (Note, for example, the large, approximately 60-fold, rate increase when crown ethers are added to oxidative-additions to tight-ion paired $Na_2Fe(CO)_4$ in THF (see Table III)). We assume that the "neutral" species is also solvent-separated, $(Na^+:S:)_2Fe(CO)_4^{2-}$.

Since cation solvation in dipolar aprotic solvents is often the predominant driving force in ion pair dissociation, the decreased rate of oxidative-addition in NMP in the presence of Bu_4NBPh_4 (Figure 5) is probably due to the equilibrium shown in Scheme IV, with $[Bu_4NFe(CO)_4]^-$ being less reactive than $[Na^+:S:Fe(CO)_4^{2-}]$.[35]

Scheme IV



The Characterization of $[Na^+:S:Fe(CO)_4^{2-}]^-$ and $Fe(CO)_4^{2-}$ as Supernucleophiles. Comparison of the nucleophilic reactivity of $[Na^+:S:Fe(CO)_4^{2-}]^-$ with other "supernucleophiles"[36] can be made using the Pearson logarithmic nucleophilicity parameter.[37] Although we have not made a direct measurement of the rate of alkylation of $[Na^+:S:Fe(CO)_4^{2-}]^-$ with methyl iodide, this rate can be reasonably estimated[38a] from the rate of an n-alkyl chloride in NMP and then correcting for methyl vs. n-alkyl[39] and chloride vs. iodide[38b] reactivity ratios. The estimated value, $n = 16.8$, is as high as any other nucleophile on record. Vitamin B_{12s} (Co(I)) and $CpFe(CO)_2^-$, previously the most reactive nucleophiles known, have $n = 14.4$ in MeOH and $n = 15.2$ (estimated[38c]) in glyme, respectively. However, the different solvents, such as protic MeOH vs. dipolar aprotic NMP, make the comparison less meaningful. The facile reaction of $Na_2Fe(CO)_4$ in NMP with the hindered substrate neopentyl bromide, $k_2 = 0.12$ M^{-1} s^{-1}, and the fact that we

Table II. Kinetic Data for Oxidative-Additions to $Na_2Fe(CO)_4$ in THF ($R = n\text{-}C_{10}H_{21}-$)

$$Na_2Fe(CO)_4 + n\text{-}RBr \xrightarrow[\text{THF}]{25.0\ °C} Na^+[RFe(CO)_4]^- + NaX$$

Entry	$10^3[Na_2Fe(CO)_4]$ (M)[a]	$10^2[C_{10}H_{21}Br]$ (M)	k_2 ($M^{-1}\ s^{-1}$)[b]	Miscellaneous
1	4.43 ± 0.55	4.84	0.104 ± 0.012[c]	
2	$Na_2Fe(CO)_4 \cdot 1.5$dioxane 5.37	4.84	0.11	$Na_2Fe(CO)_4 \cdot 1.5$dioxane was used
3	1.20	4.84	0.140	
4	0.745[d]	4.84	0.028	5.5×10^{-3} M degassed H_2O added
5	4.3	0.96	5.9	5.0×10^{-3} M dicyclohexyl-18-crown-6 added (A isomer)
6	1.0	0.214	0.52	4% (V/V) NMP/THF
7	1.0	0.16	1.9	10% (V/V) NMP/THF
8	1.0	0.16	1.1	2% (V/V) HMPA/THF
9	4.5	9.68	0.086	0.05 M $NaBPh_4$ to give $[Na^+] = 0.002$ M

[a] $[Na_2Fe(CO)_4]$ effective (see the experimental section). [b] All data at 25.0 ± 0.1 °C. [c] Standard deviation of five experiments. [d] Before H_2O addition, $[Na_2Fe(CO)_4] = 1.32 \times 10^{-3}$ M.

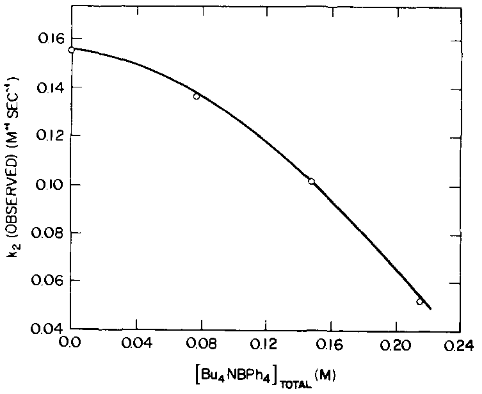


Figure 5. The effect of Bu_4NBPh_4 on: $Na_2Fe(CO)_4 + (CH_3CH_2)_2CHCH_2Cl \rightarrow Na^+[(CH_3CH_2)_2CHCH_2Fe(CO)_4]^- + NaCl$ (25.0 °C in NMP).

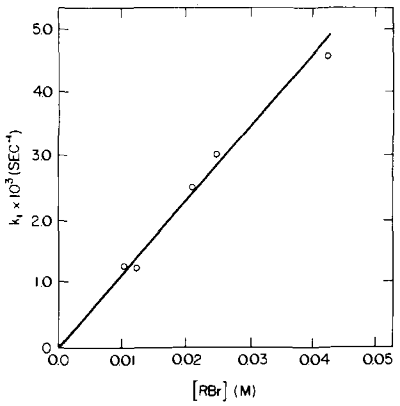


Figure 6. Linear dependence of the pseudo-first-order rate constant, k_1, on RBr concentration for ($R = n\text{-}C_{10}H_{21}-$): $Na_2Fe(CO)_4$ + RBr(excess) $\rightarrow Na^+[RFe(CO)_4]^- + NaBr$ (25.0 °C in NMP).

have even observed oxidative-addition of *neopentyl chloride*, $k_2 = 1.4 \times 10^{-5}\ M^{-1}\ s^{-1}$, document the extreme nucleophilic character of $[Na^+{:}S{:}Fe(CO)_4{}^{2-}]^-$. The estimated value for free $Fe(CO)_4{}^{2-}$ ($Na_2Fe(CO)_4$ in NMP + 2 equiv of cryptate) is 17.2, only slightly larger than $n = 16.8$ for $[Na^+{:}S{:}Fe(CO)_4{}^{2-}]^-$.

Kinetic Studies of Oxidative-Addition to $Na_2Fe(CO)_4$ in THF. In THF, $Na_2Fe(CO)_4$ is much less dissociated than in NMP, $K_{1D} \simeq 5 \times 10^{-6}$ M, $K_{2D} \ll 5 \times 10^{-6}$ M, and correspondingly less soluble (maximum solubility $\simeq 7 \times 10^{-3}$ M) and less reactive. This decreased solubility and the fact that H_2O inhibits[40] $Na_2Fe(CO)_4$ oxidative-additions make kinetic studies in THF more difficult than in NMP. In spite of these limitations, information derived from kinetic studies in THF supports the mechanism proposed in Scheme V.

The following observations are made from inspection of the data presented in Table II. As in NMP, when ion-pairing is accounted for, oxidative-addition to $Na_2Fe(CO)_4$ in THF is overall second order, first order in $Na_2Fe(CO)_4$ (entry 1, Table II) and first order in RX (Figure 6).

For the mechanism in Scheme V, with the small dissociation constant $K_{1D} \simeq 5 \times 10^{-6}$ M observed in THF, k_2(obsd) should be proportional to $1/[Na_2Fe(CO)_4]^{1/2}$ (eq (13), Scheme V). Although we have observed an increase in k_2(obsd) with decreasing $Na_2Fe(CO)_4$ concentration (entries 1, 3), the H_2O sensitivity[40] (entry 4) and insolubility of $Na_2Fe(CO)_4$ in THF preclude a more careful experimental verification of the predicted linear dependence of k_2(obsd) with $1/[Na_2Fe(CO)_4]^{1/2}$. However, the addition of polar solvents or crown ethers increases dramatically the rate of oxidative-addition, 4 and 10% (v/v)NMP/THF, giving 5- and 19-fold rate increases, respectively (entries 6, 7). HMPA is more effective than NMP, 2% (v/v) HMPA/THF giving an 11-fold rate increase (entry 8). One equivalent of the crown ether dicyclohexyl-18-crown-6 gave about a 60-fold rate increase for oxidative-addition of either *n*-alkyl bromides (entry 5) of chlorides (see Table III). *These results clearly require that the more dissociated species are kinetically more reactive; i.e., that* $k_{2-} > k_{2\pm}$ (*Scheme V*). Thus the *20 000-fold* increase in reactivity of $Na_2Fe(CO)_4$ in NMP compared to THF can be accounted for by the extent of dissociation of $Na_2Fe(CO)_4$ in the two solvents with tight ion-paired $NaFe(CO)_4{}^-$ and solvent-separated $[Na^+{:}S{:}Fe(CO)_4{}^{2-}]^-$ the kinetically dominant species in THF and NMP, respectively. It is im-

Table III. $Na_2Fe(CO)_4$ Substrate Reactivities (THF, 25.0 °C)

Substrate[a]	k_2($M^{-1}\ s^{-1}$)[b]	k_2(substrate)/k_2(RBr)
RI	5.1	51
RBr	0.10	1.0
ROTs	5.8×10^{-2}	0.58
RCl	2.3×10^{-4}	2.3×10^{-3}
RBr + crown ether[c]	5.9	59
RCl + crown ether[c]	1.2×10^{-2}	54[d]

[a] $R = n\text{-}C_{10}H_{21}-$. [b] Determined at $[Na_2Fe(CO)_4]$ effective (see experimental section) in the range (4-5.5) $\times 10^{-3}$ M. [c] One equivalent of dicyclohexyl-18-crown-6 (A isomer)/$Na_2Fe(CO)_4$. [d] k(RCl + crown ether)/k(RCl).

Table IV. Activation Parameters for Bimolecular Oxidative-Addition Reactions

System	Substrate	Solvent	$H^{\ddagger}$ (kcal/mol)	$S^{\ddagger}$ (eu)
$\mathrm{Na_2Fe(CO)_4}$	n-$\mathrm{C_{10}H_{21}Br}$	THF	7.2 ± 0.3[a]	−39 ± 5[a]
trans-$\mathrm{Ir(CO)(PPh_3)_2I}$[b]	$\mathrm{CH_3I}$	Benzene	8.8	−43
trans-$\mathrm{Ir(CO)(PPh_3)_2Br}$[b]	$\mathrm{CH_3I}$	Benzene	7.6	−46
trans-$\mathrm{Ir(CO)(PPh_3)_2Cl}$[b]	$\mathrm{CH_3I}$	Benzene	5.6	−51
trans-$\mathrm{Ir(CO)(PPh_3)_2Cl}$[b]	$\mathrm{CH_3I}$	DMF	16.4	−10
$\mathrm{Rh(C_2DOBF_2)}$[c]	n-$\mathrm{C_4H_9I}$	THF	8.0	−32

[a] Determined at five temperatures in the range 0–25 °C. Error bars represent one standard deviation from the least-squares analysis. The k_2 values (in $\mathrm{M^{-1}\,s^{-1}}$) at their respective temperatures (in °C) are: $k_2\,(24.9°) = 9.95 \times 10^{-2}$; $k_2\,(19.9°) = 8.44 \times 10^{-2}$; $k_2\,(15.0°) = 6.30 \times 10^{-2}$; $k_2\,(8.0°) = 4.41 \times 10^{-2}$; $k_2\,(0.0°) = 3.12 \times 10^{-2}$. [b] P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, **88**, 3511 (1966). [c] $\mathrm{Rh(C_2DOBF_2)}$ = {difluoro[3,3′-(trimethylenedinitrilo)di-2-pentanone dioximato]borate}rhodium(I). (See ref 5a.)

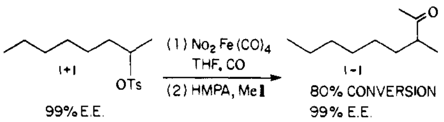
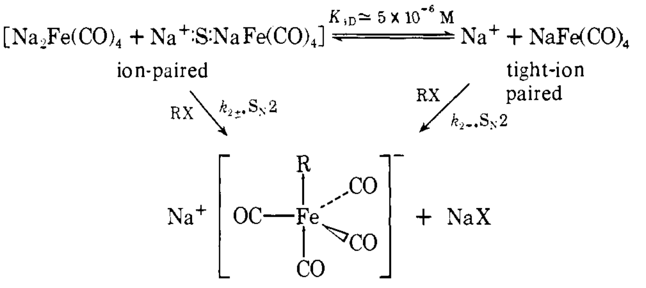


Figure 7. Observed overall stereochemistry in the oxidative-addition, migratory-insertion sequence.

portant to note that an increase of K_{1D} (Scheme V) from 5×10^{-6} M in THF to 0.24 M in NMP with tight ion-paired $\mathrm{NaFe(CO)_4^-}$ the only reactive species in both solvents (and assuming k_{2-} is the same in both solvents) *cannot* account for this 2×10^4 rate increase.[41] Furthermore, it has been shown[42] that solvent effects on k_{2-} are small—far less than that needed to account for even part of the 2×10^4 rate increase. These arguments further support our contention that the kinetically dominant species in NMP is solvent-separated $[\mathrm{Na^+{:}S{:}Fe(CO)_4{}^{2-}}]^-$.

Scheme V. Mechanism of Oxidative-Additions to $\mathrm{Na_2Fe(CO)_4}$ in THF



From Appendix 1 (in THF):

$$\frac{\mathrm{d[NaRFe(CO)_4]}}{\mathrm{d}t} = k_2(\mathrm{obsd})[\mathrm{Na_2Fe(CO)_4}]_{\mathrm{total}}[\mathrm{RX}] \quad (4)$$

where

$$k_2(\mathrm{obsd}) = (k_{2-} - k_{2\pm})\alpha + k_{2\pm} \quad (5)$$

For a small K_{1D} ($C/K_{\mathrm{1D}} \gg 1$):

$$k_2(\mathrm{obsd}) = [(k_{2-} - k_{2\pm})(K_{\mathrm{1D}})^{1/2}] \times \frac{1}{[\mathrm{Na_2Fe(CO)_4}0^{1/2}{}_{\mathrm{total}}} + k_{2\pm} \quad (13)$$

As a final proof of the dissociative equilibrium in THF, K_{1D} (Scheme V) common ion rate depression by the added $\mathrm{Na^+}$ source $\mathrm{NaBPh_4}$ was observed (entry 9), even though $\mathrm{NaBPh_4}$ is only partially dissociated in THF, K(dissociation) = 8.5×10^{-5} M.[43]

Since the complete series of relative reactivies of alkyl iodides, bromides, chlorides, and especially tosylates has been determined for only a few transition metal nucleophiles, we have examined the substrates using $\mathrm{Na_2Fe(CO)_4}$ in THF (Table III). The relative reactivities RI > RBr ~ ROTs ≫ RCl resemble classic $\mathrm{S_N2}$ reactions.[39] The facile oxidative-addition of ROTs is inconsistent with an electron-transfer/atom-abstraction component in these reactions.[44] Furthermore, the observed stereochemistry,[9b] overall inversion at carbon (Figure 7), is consistent with inversion[45] in the oxidative-addition step followed by retention in the migratory insertion step. All alkylacyl migratory insertions which have been studied using chiral carbon centers proceed with retention.[46] Stille has recently[8d] observed predominantly inversion of configuration at carbon for oxidative-addition of (R)-$\mathrm{PhCH(CF_3)(Br)}$ to $\mathrm{d^{10}}$ $\mathrm{Pd(Ph_3P)_3(CO)}$.

Activation parameters for oxidative-addition of n-bromodecane to $\mathrm{Na_2Fe(CO)_4}$ in THF were also determined.[47] The values obtained, $\Delta H^{\ddagger} = 7.2 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = -39 \pm 5$ eu, are similar to those for other bimolecular oxidative-addition reactions that are thought to proceed via a $\mathrm{S_N2}$ mechanism (Table IV) and are characterized by low $\Delta H^{\ddagger}$ and large negative $\Delta S^{\ddagger}$ values.

Thus the observed stereochemistry, rate law, substrate reactivities (RI > RBr ~ ROTs ≫ RCl), activation parameters, and the fact that the more dissociated species are more reactive ($k_{2-} > k_{2\pm}$) are all consistent with a $\mathrm{S_N2}$ mechanism of oxidative-addition to $\mathrm{Na_2Fe(CO)_4}$ in THF. As mentioned previously, earlier studies indicate that d^n (n = even) transition metal nucleophiles often show a facile two-electron ($\mathrm{S_N2}$) oxidative-addition mechanism with a competing one-electron mechanism. The fact that $\mathrm{Na_2Fe(CO)_4}$ shows no detectable competing one-electron mechanism makes it a model system for study of the two-electron ($\mathrm{S_N2}$) oxidative-addition mechanism.

One further interesting observation can be made concerning the relative substrate reactivities in Table III. Hoffman[48] and Depuy[49] have argued that reactions with low $k_{\mathrm{ROTs}}/k_{\mathrm{RBr}}$ ratios imply a high degree of bond making in the transition state which precedes bond breaking and charge separation between carbon and its leaving group. Observed ratios range from 0.36 to 5000 for thiolate displacements on methyl bromides and tosylates to $\mathrm{E_1}$ reactions of *tert*-butyl bromides and tosylates, respectively.[48] The low value shown by $\mathrm{Na_2Fe(CO)_4}$ in THF $k_{\mathrm{rots}}/k_{\mathrm{RBr}} = 0.58$, is very similar to the 0.63 value for $\mathrm{S_N2}$ reactions of a thiolate anion in EtOH[48] (Figure 8), and shows that the transition state of $\mathrm{Na_2Fe(CO)_4}$ in THF $\mathrm{S_N2}$ reactions requires relatively little charge separation between carbon and its leaving group.

Since the chemistry of $\mathrm{Na_2Fe(CO)_4}$ is dominated by ion-pairing effects, it was of interest to see if $\mathrm{Na_2Fe(CO)_4}$ displayed the salt effects unique to ion-pairing systems. Addition of $\mathrm{Bu_4NBPh_4}$, which is ~90% ion-paired at 0.004 M in THF, K(dissociation) = 4.3×10^{-5} M,[43] gave a linear increase in

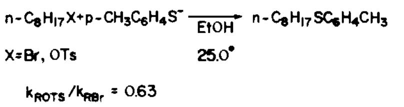


Figure 8. k_{ROTs}/k_{RBr} ratio for S_N2 reactions of the thiolate nucleophile.

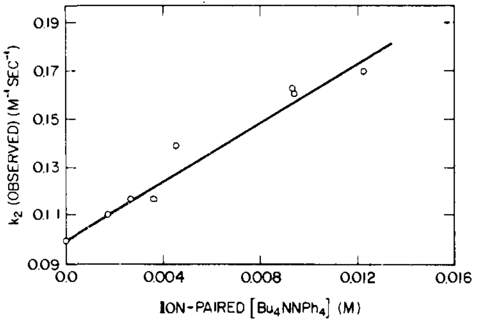


Figure 9. The effect of added Bu_4NBPh_4 on the rate of (R = n-$C_{10}H_{21}$-): $Na_2Fe(CO)_4$ + RBR → $Na^+[RFe(CO)_4]^-$ + NaBr (25.0 °C in THF).

k_2(obsd) with the amount of ion-paired Bu_4NBPh_4 (Figure 9).

$$k_2(\text{obsd}) = (5.8 \pm 0.5)[(Bu_4NPPh_4)_{\text{ion-paired}} + (0.10 \pm 0.01)]$$

Winstein called this the normal salt effect, and suggested it is due to electrophilic assistance to ionization.[50] A statistical mechanical model for the normal salt effect has also appeared.[51]

Oxidative-Additions to the Dioxane Solvate $Na_2Fe(CO)_4$· 1.5dioxane. Although $Na_2Fe(CO)_4$ has been used throughout this work, due to the development of a more convenient, large-scale preparation of $Na_2Fe(CO)_4$·1.5dioxane[52] and its commercial availability,[53] the kinetics of oxidative-addition to the dioxane solvate were examined. Even though immediately after dissolution $Na_2Fe(CO)_4$·1.5dioxane is ~13 times more soluble in THF than $Na_2Fe(CO)_4$, it reacted with n-bromodecane at a rate identical with that of the nonsolvated $Na_2Fe(CO)_4$ (entry 2, Table II). Dissolution of $Na_2Fe(CO)_4$·1.5dioxane in THF followed by precipitation with petroleum ether gave 96% pure $Na_2Fe(CO)_4$ (no solvate). These results and the fact that in all the reactions examined,[10] $Na_2Fe(CO)_4$·1.5dioxane behaves identically with $Na_2Fe(CO)_4$, suggests that the solution nature of the two reagents is identical.

Ion-Pairing in the Solid State. The Crystal Structures of $Na_2Fe(CO)_4$·1.5dioxane, (cryptate·Na^+)$Fe(CO)_4^{2-}$, and $K_2Fe(CO)_4$. What is the nature of the cation binding site(s) in the $Fe(CO)_4^{2-}$? A model for the unperturbed, d^{10}, $Fe(CO)_4^{2-}$ moiety is isoelectronic $Ni(CO)_4$. A number of IR and Raman spectral studies show that $Ni(CO)_4$ is tetrahedral.[54] Previous infrared studies of the isoelectronic system, $NaCo(CO)_4$, showed a pattern of ν_{CO} frequencies consistent with a C_{3v} symmetry structure in low polarity solvents like THF (E and F, Figure 10). Since possible solution ion-binding sites in $Co(CO)_4^-$ had already been studied, we chose to further characterize interactions between cations and the isoelectronic $Fe(CO)_4^{2-}$ dianion by solid state structural analysis. Single-crystal X-ray diffraction structures of (cryptate·Na^+)$_2$-$Fe(CO)_4^{2-}$, $K_2Fe(CO)_4$, and $Na_2Fe(CO)_4$·1.5dioxane have appeared elsewhere,[55,56] and will only be briefly discussed here.

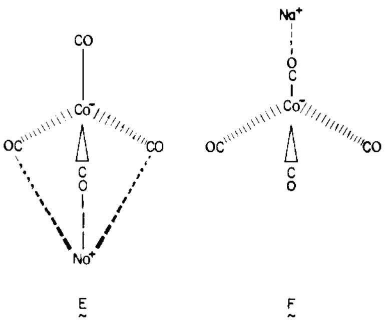


Figure 10. Possible $NaCo(CO)_4$ structures of C_{3v} symmetry.

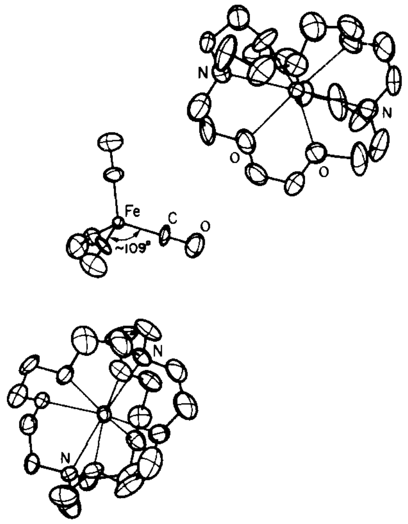


Figure 11. Complete molecular plot of [cryptate·Na^+]$_2Fe(CO)_4^{2-}$, showing the two [cryptate·Na]$^+$ cations and the $Fe(CO)_4^{2-}$ anion.

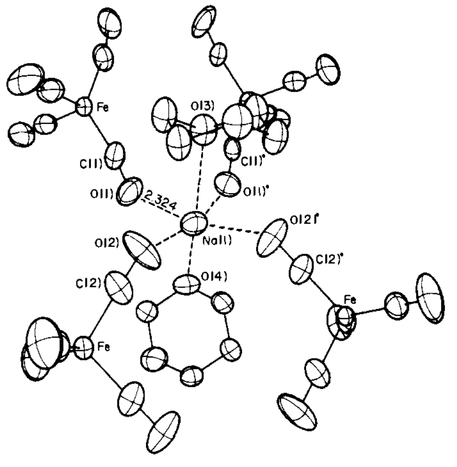


Figure 12. The coordination about NA(1)$^+$ in $Na_2Fe(CO)_4$·1.5dioxane. Oxygen atoms from four different $Fe(CO)_4^{2-}$ groups and two dioxane molecules make up an approximately octahedral coordination sphere about Na(1)$^+$.

The structure[55] of (cryptate·Na^+)$_2Fe(CO)_4^{2-}$ shows an essentially undistorted, tetrahedral $Fe(CO)_4^{2-}$ unit, as expected for a four-coordinate, d^{10} system (Figure 11). The IR (KBr) of (cryptate·Na^+)$_2Fe(CO)_4^{2-}$ shows a single broad ν_{CO} band (1720 cm^{-1}) as expected for T_d symmetry. However, Bau has found that, in the structure[56] of $Na_2Fe(CO)_4$·1.5dioxane, two types of interactions between the Na^+ cations and $Fe(CO)_4^{2-}$ significantly distort the $Fe(CO)_4^{2-}$ unit (Figures 12 and 13). Notably, long range Na(2)$^+$···C and Na(2)$^+$···Fe interactions (2.95 and 3.09 Å, respectively) are probably responsible for the distortion of one C-Fe-C angle to 129.7°. Shorter range Na(1)$^+$···O interactions (2.32 Å) also

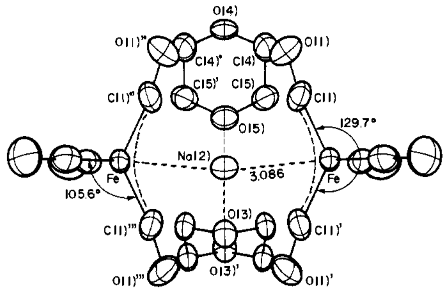


Figure 13. The coordination about $Na(2)^+$ in $Na_2Fe(CO)_4 \cdot 1.5$dioxane. The dioxane molecules are below the plane of the diagram and two $Fe(CO)_4{}^{2-}$ groups are above the plane of the diagram.

occur. In the $K_2Fe(CO)_4$ structure,[55] again there is an association of the alkali metal ion with the C–Fe–C region of $Fe(CO)_4{}^{2-}$. The $K^+ \cdots Fe$ distance (3.62 Å) is significantly larger than the $Na^+ \cdots Fe$ distance, suggesting a weaker $M^+ \cdots Fe$ interaction. This interpretation is consistent with the lower degree of angular distortion in $K_2Fe(CO)_4$ (one C–Fe–C angle = 121.0°). These solid state structural results are not directly applicable to the structure of $Na_2Fe(CO)_4$ in solution. However, they are consistent with the solution IR studies on $NaCo(CO)_4$, and strongly indicate that $Fe(CO)_4{}^{2-}$ has at least two types of ion-binding sites (Figure 10) in THF.

Summary and Conclusions

Mechanistic studies continue to be important to the development of organometallic chemistry. Herein we have presented kinetic and mechanistic results from oxidative-additions of alkyl halides and tosylates to $Na_2Fe(CO)_4$ in both THF and NMP. Ion-pairing effects which dominate $Na_2Fe(CO)_4$ oxidative-additions give a 2×10^4 rate increase in NMP vs. THF.

In NMP, $Na_2Fe(CO)_4$ is dissociated into predominantly solvent-separated $(Na^+{:}S{:}Fe(CO)_4{}^{2-})^-$, $K_{1D} = 0.24 \pm 0.04$ M with little dissociation to free $Fe(CO)_4{}^{2-}$, 10^{-3} M $\geq k_{2D} \geq 10^{-5}$ M. Supernucleophilic $(Na^+{:}S{:}Fe(CO)_4{}^{2-})^-$ is the kinetically dominant species in NMP and is ≥ three times as reactive as ion-paired $(Na^+{:}S{:})_2Fe(CO)_4{}^{2-}$ while free $Fe(CO)_4{}^{2-}$ is not kinetically important. All of our data support an S_N2 mechanism of oxidative-addition to $Na_2Fe(CO)_4$ in NMP, with no detectable competing one-electron mechanism.

In THF, $Na_2Fe(CO)_4$ (or $Na_2Fe(CO)_4 \cdot 1.5$dioxane) is much less dissociated than in NMP, with ion-paired $Na_2Fe(CO)_4$ (and/or $Na^+{:}S{:}NaFe(CO)_4{}^-$) the predominant solution species ($K_{1D} \simeq 5 \times 10^{-6}$ M), with essentially no dissociation to free $Fe(CO)_4{}^{2-}$ ($K_{2D} \ll 5 \times 10^{-6}$ M). As in NMP, in THF the more dissociated species are kinetically more active. Tight-ion paired $NaFe(CO)_4{}^-$ is the kinetically dominant species. The observed stereochemistry at carbon, the rate law, substrate reactivities (RI > RBR > ROTs ≫ RCl), activation parameters (especially the large negative entropy of activation), and the fact that the more dissociated species are more reactive are all consistent with an S_N2 oxidative-addition mechanism in THF, again with no detectable competing one-electron mechanism. $Na_2Fe(CO)_4$ in THF also displays the "normal" salt effect unique to ion-pairing systems. Single-crystal x-ray diffraction structure determinations of various alkali metal cation and cryptated cation salts of $Fe(CO)_4{}^{2-}$ have been used to determine the extent of "ion-pairing" to $Fe(CO)_4{}^{2-}$ in the solid state and to suggest possible $Fe(CO)_4{}^{2-}$ cation binding sites in solution.

In subsequent publications, we will present our now completed mechanistic work[21f] on the alkyl-acyl migration and ketone producing reactions of $RFe(CO)_4{}^-$ as well as synthetic and mechanistic studies of the selective reduction of the olefinic bond in α,β-unsaturated carbonyl compounds using the binuclear hydride $NaHFe_2(CO)_8$.[57]

Experimental Section

(A) General. (i) Methods for Handling Air-Sensitive Compounds. Air and water free conditions were maintained at all times throughout this work.[58] $Na_2Fe(CO)_4$, all solvents, alkyl halides, etc., were stored in and preparation of solutions were carried out in a Vacuum Atmospheres Co. inert atmosphere (nitrogen) drybox. The level of oxygen and water impurities in the drybox was monitored using Et_2Zn or a light bulb and was ≤1 ppm. The Et_2Zn fumed in the presence of ≥5 ppm O_2, H_2O, R_3N, or ROH, while a light bulb with a small hole in it generally burned for 2 to 3 weeks indicating ≤1 ppm impurities. All flasks and vials used in the kinetic experiments were dried at 140 °C overnight, then held under vacuum followed by cooling under nitrogen. Liquid transfers outside the drybox were handled by syringe and needle-stock techniques. Nitrogen (99.996%) was further purified by passage through a BASF oxygen scavenger and Linde 3A molecular sieve.

(ii) **Equipment.** IR spectra were recorded on a Perkin-Elmer 457 grating infrared spectrophotometer. NMR spectra were taken on a Varian T-60 spectrometer. Conductivity measurements were made using either a Yellow Springs Instruments Model 31 conductivity bridge or an Industrial Instruments Model RC 13B2 bridge, and a Yellow Springs Model 3403 dip cell (cell constant = 1.0). "Gastight" Hamilton Co. syringes were used throughout this work. Those used for quantitative transfers were calibrated to ±5%. Injections into the flame GLC were made using a no. 7101 NCh 1.0 "microliter" syringe. Temperature control was maintained with a Forma-Temp Jr. constant temperature bath, and was monitored using a 76-mm immersion thermometer calibrated from −1 to 101 °C by 0.1° (VWR Scientific Co., no. 61032).

(iii) **Gas-Liquid Chromatography.** Reactions were monitored by injection, without workup, of the crude reaction mixtures into a Hewlett-Packard Model 5750 gas chromatograph with flame ionization detector. All reactions were analyzed using either a Hi-Pak column (Hewlett-Packard no. S-5750-6-3840, 6 ft by ⅛ in. stainless steel, packed with UCW 98 silicone gum on AW-DMCS Chromosorb W) or a 6 ft by ⅛ in. stainless steel column hand-packed with 10% OV-101 on 80/100 mesh AW-DMCS (Supelco, Inc.). Peaks were identified by coinjection. Internal standards and detector response correction factors based on injection of known amounts of pure compounds were used throughout this work. Quantification was by Vidar 6300 digital integrator or, for very sharp peaks, by peak heights.

(B) Materials. (i) General. $Fe(CO)_5$ (Pressure Chemical Co.) was filtered and stored in a dark bottle under nitrogen over Linde 4A Molecular Sieves. Sodium dispersion (50% in paraffin) was obtained from Matheson, Coleman and Bell Chemical Co. The outer layer was scraped off and the inner layer was used. $NaBPh_4$ and galvanoxyl free radical were purchased from Aldrich. Bu_4NBPh_4 (mp 232–235 °C, lit. 233–235 °C) was prepared by mixing 2% H_2O solutions of $NaBPh_4$ and Bu_4NBr, collecting the Bu_4NBPh_4, washing with H_2O, and recrystallizing from 2:1 acetone/H_2O (200 mL/g). Bu_4NBPh_4 and $NaBPh_4$ were dried (Abderhalden pistol-P_2O_5) and stored in the drybox.

(ii) **Solvents.** THF was doubly distilled under nitrogen, first from CaH_2 in a recirculating still, then from sodium/benzophenone into a flame dried flask. Reagent grade NMP and HMPA were refluxed at reduced pressure over CaH_2 for at least 2 days, followed by vacuum distillation into a flame dried flask containing activated 3A or 13X molecular sieve. All solvents were stored in the drybox after bubbling the drybox atmosphere (>1 ppm O_2) through them for 15 min.

(iii) **Preparation of $Na_2Fe(CO)_4$.** In a dry 2-L round-bottom flask having a gas inlet side arm and fitted with a serum stopper were placed 9.2 g (0.2 mol) of a 50% sodium dispersion, 1.7 g (0.01 mol) benzophenone, and a magnetic stir bar. The flask was flushed with nitrogen, connected to an oil bubbler, and 1.2 L of dry (Na/benzophenone) THF was added via needle-stock technique giving a deep purple solution. The rapidly stirred solution was titrated with $Fe(CO)_5$ (approximately 13.4 mL, 0.1 mol) added using a syringe. In the early stages of the reaction, the $Fe(CO)_5$ was added as rapidly as possible while still maintaining the purple to blue color of the benzophenone ketyl. (Having the ketyl in excess prevents the reaction $Na_2Fe(CO)_4 + Fe(CO)_5 \rightarrow Na_2Fe_2(CO)_8 + CO$.) In the later stages of the reaction, the blue color was discharged with $Fe(CO)_5$, the reaction stirred until the blue color had fully developed, the blue color again discharged, etc. White $Na_2Fe(CO)_4$ precipitated after ca. 10 mL of $Fe(CO)_5$ was added, after which the blue color returned more slowly. (Often, very slow addition of the final few milliliters of $Fe(CO)_5$ with stirring over 2–3 days was required to produce very white $Na_2Fe(CO)_4$ without visible Na remaining.)

Caution: $Fe(CO)_5$ is toxic and CO is rapidly evolved, so the reaction should be carried out in a hood and gloves should be worn.

When the reaction remained tan and the blue-green color would not return, precipitation was completed by the addition via needlestock of 600 mL of dry hexane (distilled from CaH_2 under nitrogen). The brown supernatant was decanted under positive N_2 flow. The precipitate was washed with a second portion of hexane (500–750 mL) and decanted. A third washing (500–750 mL) was removed through a fritted glass (gas bubbler) tube under positive nitrogen pressure. The remaining solvent was removed under vacuum giving 18.7 g (88%) of white powdered pyrophoric $Na_2Fe(CO)_4$, which was double bottled and stored in the drybox over $Na_2Fe(CO)_4$ in the outer bottle as an oxygen scavenger. High purity product was characterized by a white color (all known multinuclear iron by-products are highly colored) and the lack of remaining visible Na. The product purity was further assessed by determining the amount of nonanal produced from a known weight of $Na_2Fe(CO)_4$ and excess octyl bromide. This reaction had previously been shown to give a quantitative yield of aldehyde with a slight excess of $Na_2Fe(CO)_4$.[9a] All $Na_2Fe(CO)_4$ used in this work had a 100 ± 5% aldehyde titer. Trimesityl boron can be used in place of benzophenone as an electron carrier, and, occasionally, gave better results.

(iv) **$Na_2Fe(CO)_4$ Aldehyde Titer.** In the drybox, 214 mg of $Na_2Fe(CO)_4$ (1.0 mmol), 320 mg of recrystallized, dried PPh_3 (1.26 mmol), 10 mL of THF, 208 μL of octyl bromide (1.2 mmol), and a magnetic stir bar were added to a 25-mL Erlenmeyer flask, which was fitted with a rubber septum and removed from the drybox. After 2 h, 250 μL of glacial acetic acid and 100 μL of dodecane internal standard were added by syringe. The crude reaction mixture was analyzed by GLC using detector response correction factors.

(v) **Preparation of $K_2Fe(CO)_4$.** $K_2Fe(CO)_4$ was prepared in a manner exactly analogous to $Na_2Fe(CO)_4$, except for the following changes. Potassium sticks in mineral oil were freed of their oxide coating using the following procedure due to Depuy.[59] A stick of potassium was placed in dry, degassed benzene under nitrogen, and heated gently until the potassium melted. With gentle swirling, molten potassium eggs free of oxide were formed. After cooling, the required amount of purified potassium was transferred under nitrogen to a 2-L round bottom. $Fe(CO)_5$ was added and the resultant $K_2Fe(CO)_4$ worked up as described for $Na_2Fe(CO)_4$. The resultant light tan $K_2Fe(CO)_4$ powder is insoluble in THF, so an alkane titer in NMP was used. Addition of octyl bromide to a NMP solution of $K_2Fe(CO)_4$ followed by acid quench and GLC analysis of the resultant octane required the $K_2Fe(CO)_4$ be ca. 90% pure. Further purification was achieved by recrystallization from MeOH–THF. Due to the lower air sensitivity of $K_2Fe(CO)_4$ vs. $Na_2Fe(CO)_4$, a satisfactory elemental analysis was obtained. Anal. Calcd for $K_2Fe(CO)_4$: K, 31.7; Fe, 22.6; C, 19.5; (H, 0). Found: K, 31.7; Fe, 22.5; C, 19.75; (H < 0.2).

(vi) **Alkyl Halides and Tosylates.** Alkyl halides and tosylates were either purchased (Aldrich) or prepared by standard methods. Liquid alkyl halides were distilled under nitrogen from P_2O_5 prior to use, and stored in dark bottles. Alkyl iodides, stored in contact with a clean copper wire to prevent iodine buildup, were passed through a plug of alumina in the drybox immediately prior to their use. *n*-Alkyl tosylates were purified by high vacuum bulb-to-bulb distillation.

(vii) **Crown Ethers and Cryptands.** The cryptand,[23] Kryptofix 222, was purchased from E. Merck Laboratories, Inc., and used as received. Dicyclohexyl-18-crown-6 (Aldrich), received as a crude mixture of the A and B isomers, was purified by chromatography on neutral alumina. Only the isomer, mp 60.0–62.0 °C (lit. mp 61–62.5 °C) was used in this work. A better method for purification of dicyclohexyl-18-crown-6 has been published.[60]

(C) Kinetics. Central to the kinetic method employed was the acid quench (glacial HOAc or concentrated HCl). Normally, a two- to tenfold excess of H^+/iron was used. The immediate color change accompanying acid quench of $NaRFe(CO)_4$/NMP solutions and the well-behaved nature of the kinetic data, imply that the quench reaction is very rapid on the time scale of the $Na_2Fe(CO)_4$ oxidative-addition reactions studies.

(i) **Kinetics of $Na_2Fe(CO)_4$ Oxidative-Additions in NMP.** These reactions were usually run pseudo-first-order with $Na_2Fe(CO)_4$ in excess using the one vial–one kinetic point technique. First-order log plots were linear over at least three half-lives. The NMP kinetics were very clean, repetitive runs often agreeing within 5%, and are probably precise to within ±15%. However, the very fast reaction of *n*-hexyl chloride and very slow reaction of neopentyl chloride ($k_2 = 5.0$ and $1.4 \times 10^{-5}\ M^{-1}\ \mathrm{sec}^{-1}$, respectively), although reproducible, are probably less accurate. The following illustrates a typical $Na_2Fe(CO)_4$/NMP kinetic experiment. In the drybox, 20.0 mL of NMP was pipetted into a 25-mL Erlenmeyer containing 257 mg of $Na_2Fe(CO)_4$ (0.06 M) and a stirbar. After a few minutes of stirring, 2.0 mL of the resultant light yellow homogeneous solution was placed into each of nine 2-dram vials via syringe, which were then capped with new, washed rubber septa. The vials were removed from the drybox, suspended in a constant temperature bath, and allowed to come to thermal equilibrium. The reaction was started by injection of a measured amount of stock solution of NMP, alkyl halide, and suitable hydrocarbon internal standard, with vigorous swirling to ensure good mixing. At suitable intervals covering 10 to ca. 90% reaction, a vial was quenched by the injection of a two- to tenfold excess of glacial HOAc or concentrated HCl. A zero-time vial was obtained by quenching with acid first, then adding the measured amount of the alkyl halide–hydrocarbon internal standard solution. The disappearance of reactants (measured as alkyl halide) and appearance of products (measured as alkane) were simultaneously analyzed using GLC, giving two values of the rate constant for each kinetic run. Furthermore, good material balance was obtained, since the ratio of moles of reactant consumed/moles of product formed was found to be 1.0 ± 0.1 for all the reactions studied. Faster reactions (e.g., *n*-hexyl chloride) were run under second-order conditions.

(ii) **Determination of Effective $Na_2Fe(CO)_4$.** It was found that a determination of the active $Na_2Fe(CO)_4$ for each run in NMP was necessary to give rate constants consistent to ±5–10% probably due to the presence of adventitious H_2O and O_2. In NMP the effective $[Na_2Fe(CO)_4]$ was determined by adding a known excess amount of alkyl halide and determining the percent consumed by GLC. The $[Na_2Fe(CO)_4]$ (effective) was then calculated by $[Na_2Fe(CO)_4]_{\mathrm{effective}} = [RX] \cdot (\%\ \mathrm{consumed})$, and used to calculate $k_2(\mathrm{obsd}) = k_1/[Na_2Fe(CO)_4]_{\mathrm{effective}}$. In THF, since the reactions were generally run pseudo-first-order with RX in excess, and $k_2(\mathrm{obsd}) = k_1/[RX]$, the $[Na_2Fe(CO)_4]$ effective was monitored simply as a quality check on each kinetic run. The effective $[Na_2Fe(CO)_4]$ was determined using the following equation:

$$[Na_2Fe(CO)_4]_{\mathrm{effective}} = (\mathrm{M\ internal\ standard}) \left(\frac{\mathrm{area\ product}}{\mathrm{area\ standard}}\right) \times (\mathrm{response\ correction\ factor})$$

(iii) **Kinetics of Oxidative-Additions in THF.** Since $Na_2Fe(CO)_4$ is only slightly soluble in THF, these reactions were unusually performed pseudo-first-order in RX using an aliquot technique. (The more reactive alkyl iodides were run under second-order conditions, $[RI] \simeq 2[Na_2Fe(CO)_4]$ effective.) Therefore, only the appearance of products (measured as alkane) was monitored. First-order log plots were generally linear over ca. 1.5 half-lives. Repetitive kinetics runs were reproducible to within 10 to 15%. For the kinetic studies in THF, a standard solution of $Na_2Fe(CO)_4$ plus internal standard was prepared as follows. In the drybox, 310 mg of $Na_2Fe(CO)_4$ and 265 mL of THF (5.4×10^{-3} M) were placed in a dry 500-mL round-bottom flask and stirred for a few hours; 250 mL of the resultant light tan homogeneous solution was transferred by pipette to a dry brown bottle and 250 μL of undecane internal standard was added. This solution was stored tightly capped in the drybox, and used within 1 week, since a noticeable decrease in the $[Na_2Fe(CO)_4]_{\mathrm{effective}}$ occurred within 2 weeks. The kinetic results were reproducible between different standard solutions. An example of a typical THF kinetic run is as follows: 10 mL of the standard $Na_2Fe(CO)_4$ solution was pipetted into a dry 25-mL Erlenmeyer which was capped with a rubber septum and removed from the drybox. After thermal equilibration in the constant temperature bath, the reaction was started by injecting a measured amount of RX and vigorous shaking. At six or seven intervals covering 10 to 75% reaction, a 150-μL aliquot was removed using a gas-tight syringe, and injected into a nitrogen filled, septum capped, 6 × 50 mm culture tube containing 5 mL of HOAc. Two infinity points (at ≥10 half-lives) were also taken and were analyzed for product (e.g., decane) and hydrocarbon standard (usually undecane) by GLC.

(iv) Analysis of the Kinetic Data. Most of the kinetic studies were run under pseudo-first-order conditions. In NMP the concentrations of both the starting material and product could be simultaneously measured by GLC, giving two values for the pseudo-first-order rate constant, k_1, in each run. These rate constants were found by fitting the data to one of two basic equations, one for the loss of reactant (eq I) and one for increase in product (eq II). In these equations, R_0 and R_t are the concentrations of reactant at time zero and t, respectively, while P_∞ and P_t are the concentrations of product at infinity (completion) and t, respectively.

$$\ln (R_0/R_t) = k_1 t \qquad \text{(I)}$$

$$\ln (P_\infty/(P_\infty - P_t)) = k_1 t \qquad \text{(II)}$$

Since all the reactions studied went cleanly to completion, with no observable equilibria or significant side reactions, these simple equations handled the data very well. In THF, since alkyl halide was used in pseudo-first-order excess, only eq II was used. The second-order rate constant, k_2, was found by dividing k_1 by the concentration of the excess reactant.

For second-order reactions run under conditions where A_0 differs from B_0 by at least a factor of 2 but less than a factor of 5, eq III was used. B_0, A_0 and B_t, A_t are the concentrations of reactant B and A, respectively, at times zero and t, respectively. The change in concentration of one reactant was measured; from this and the reaction stoichiometry, the change in concentration of the other reactant was calculated, and eq III was used. Simple computer programs, written in interactive BASIC and run in the time-sharing mode on the Stanford IBM 360/67 computer, were used to find the least-squares line and correlation coefficient using eq I, II, and III.

$$\frac{1}{B_0 - A_0} \ln \left[\frac{A_0(B_t)}{B_0(A_t)}\right] = k_2 t \qquad \text{(III)}$$

The second-order polynomial least-squares fit to the k_2(obsd) vs. $[Na_2Fe(CO)_4]$ in NMP data was performed using a generalized polynomial least-squares curve-fitting routine.[62]

(D) Conductometric Titrations and Equivalent Conductances vs. Dilution Experiments. These experiments were performed in the drybox at 25 ± 2 °C, with the conductivity cell connected via wire leads to a bridge outside the drybox. In the conductometric titration of a 0.095 M $Na_2Fe(CO)_4$/NMP solution with Kryptofix 222, 150-μL aliquots of a 0.56 M Kryptofix 222/NMP solution were added to the $Na_2Fe(CO)_4$/NMP solution, and conductance readings were taken after the addition of each aliquot, and corrected for dilution.

For the equivalent conductance vs. dilution experiment in THF, extra care was taken to avoid adventitious H_2O. All glassware used in this experiment was flamed twice with cooling overnight under vacuum. Five serial dilutions of an originally 6.0×10^{-3} M $Na_2Fe(CO)_4$/THF solution were made in the drybox, yielding the most dilute solution at $(6.0/32) = 1.87 \times 10^{-3}$ M $Na_2Fe(CO)_4$. Starting with the most dilute solution, the conductance at each dilution was measured.

(E) Cryoscopic Molecular Weight Measurements. (i) Apparatus. The apparatus and methods used in these experiments were adapted from Shoemaker and Garland.[61] A three-way stopcock was added to their cryoscopic molecular weight apparatus for solution additions and a continuous nitrogen flow. Instead of a cork stopper in the top, a large rubber serum cap with a tight fitting hole for the Beckman thermometer and a smaller, looser hole for the stirrer and nitrogen outlet was used.

(ii) Calibration of NMP as a Cryoscopic Melting Point Solvent. The apparatus was thoroughly flushed with nitrogen and cooled in a bromobenzene slush bath (−30.95 °C) until the Beckman thermometer was cold enough for a rough setting. A flow of nitrogen through the apparatus was continued throughout the run. Cold NMP was then added via needlestock; its weight was found by difference in the storage flask. The thermometer was then finally set, and the freezing point of the pure NMP measured. Its tendency to supercool required careful cooling until it froze, rewarming to about 1° above the freezing point with vigorous stirring, and then recooling.

An aliquot of a solution of standard compound in NMP was then added via syringe to the NMP in the apparatus; the solution was mixed well and the new melting point was taken. This was repeated at least twice with successive aliquots. The relative melting point was plotted vs. the molality of the standard compound to determine the molal cryoscopic constant of NMP.

(iii) Naphthalene. The standard solution was made up of napthalene (510 mg, 4.0 mmol) in 5.0 mL of NMP. Successive 1.50-mL of aliquots were added to the original quantity of 28.97 g of NMP. The cryoscopic constant was 5.0 ± 0.3 deg mol^{-1}.

(iv) Sodium Thiocyanate. The solution of NaSCN was made up of dried NaSCN (0.281 g, 3.47 mmol) in 5.0 mL of NMP. Successive aliquots of 0.5, 0.75, 1.00, and 1.00 mL of the solution were added to the original 36.25 g of NMP. The cryoscopic constant was 8.4 ± 0.5 deg mol^{-1}.

(v) 1,4-Diaza-1,4-dimethylbicyclo[2.2.2]octane Diiodide (DMDI). The solution of DMDI was made up of DMDI (800 mg, 2.0 mmol) in NMP (25.0 mL). Three successive 5.0-mL aliquots were added to the original quantity of NMP (30.88 g). The cryoscopic constant was 15.0 ± 0.9 deg mol^{-1}.

(vi) Cryoscopic Molecular Weight of $Na_2Fe(CO)_4$. The technique used for the standardization runs was used for $Na_2Fe(CO)_4$. Two runs were made. In the first, a solution of $Na_2Fe(CO)_4$ (370 mg, 1.75 mmol) in NMP (6.15 g) was used; three successive 1.0-mL aliquots were added to the original quantity of NMP (28.92 g). In the second, a solution of $Na_2Fe(CO)_4$ (428 mg, 2.0 mmol) in 5.0 mL of NMP was used; three 1.0-mL and one 1.5-mL aliquots were added to the original quantity of NMP (35.55 g). The cryoscopic constants found were 8.9 ± 0.9 and 8.5 ± 0.3 deg mol^{-1}.

Acknowledgement. We wish to thank Professor R. M. Fuoss for a preprint of unpublished materials and helpful suggestions. This work was supported by the National Science Foundation, Grant No. CHE75-17018.

Appendix I. Derivation of Kinetic Equations

(A) In NMP, for the mechanism of Scheme III (neglecting activity coefficients):

$$K_{ID} = \frac{[Na^+][(Na^+{:}S{:}Fe(CO)_4{}^{2-})^-]}{[(Na^+{:}S{:})_2Fe(CO)_4{}^{2-}]}$$

$$= \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \qquad (1)$$

where

$$C \equiv [Na_2Fe(CO)_4]_{total}$$

$$\alpha \equiv \text{degree of dissociation}$$

From eq 1, α is a quadratic in K_{ID}, C:

$$\alpha = \left(\frac{-1 \pm 1 + 4C/K_{ID})^{1/2}}{2C/K_{ID}}\right) \qquad (2)$$

$$\frac{d[NaRFe(CO)_4]}{dt} = [k_{2\pm}C(1-\alpha) + k_{2-}C\alpha][RX] \qquad (3)$$

$$= k_2(\text{obsd})[Na_2Fe(CO)_4]_{total}[RX] \qquad (4)$$

where

$$k_2(\text{obsd}) = (k_{2-} - k_{2\pm})\alpha + k_{2\pm} \qquad (5)$$

For a large K_{ID} and small $[Na_2Fe(CO)_4]_{total}$, the square root term may be expanded as a power series[29b] which converges absolutely for $|x| < 1$:

$$(1+x)^{1/2} = 1 + \tfrac{1}{2}x - \frac{1\cdot 1}{2\cdot 4}x^2 + \frac{1\cdot 1\cdot 3}{2\cdot 4\cdot 6}x^3 - \frac{1\cdot 1\cdot 3\cdot 5}{2\cdot 4\cdot 6\cdot 8}x^4 + \ldots \qquad (6)$$

Using $x = 4C/K_{ID}$ and taking the positive square root, one obtains eq 7:

$$\alpha = 1 - \frac{C}{K_{ID}} + \frac{2C^2}{K_{ID}{}^2} - \frac{5C^3}{K_{ID}{}^3} + \ldots \qquad (7)$$

To first order, α decreases linearly with concentration, eq 8:

$$\alpha \simeq 1 - \frac{C}{K_{1D}} \tag{8}$$

Now eq 8 substituted in eq 5 yields eq 9:

$$k_2(\text{obsd}) \simeq -(k_{2-} - k_{2\pm}) \frac{[\mathrm{Na_2Fe(CO)_4}]_{\text{total}}}{K_{1D}} + k_{2-} \tag{9}$$

Where eq 9 holds if K_{1D} is large and $[\mathrm{Na_2Fe(CO)_4}]_{\text{total}}$ is small.

(B) In THF, for the mechanism of Scheme V:

$$K_{1D} = \frac{[\mathrm{Na^+}][\mathrm{NaFe(CO)_4^-}]}{[\mathrm{Na_2Fe(CO)_4}] + [\mathrm{Na^+{:}S{:}NaFe(CO)_4^-}]} = \frac{C\alpha^2}{1-\alpha} \tag{10}$$

Where, if we consider the equilibria:

$$\mathrm{Na_2Fe(CO)_4} \overset{K_1}{\rightleftharpoons} \mathrm{Na^+{:}S{:}NaFe(CO)_4^-}$$

$$\overset{K_2}{\rightleftharpoons} \mathrm{Na^+} + \mathrm{NaFe(CO)_4^-} \qquad K_{1D} = \frac{K_1K_2}{1+K_1} \tag{11}$$

Now in THF, K_{1D} is small. For a small K_{1D} and large $[\mathrm{Na_2Fe(CO)_4}]_{\text{total}}$ (i.e., small α, $4C/K_{1D} \gg 1$) eq 2 becomes eq 12:

$$\alpha \approx \left(\frac{K_{1D}}{C}\right)^{1/2} \tag{12}$$

And the expected rate law in THF becomes:

$$\frac{\mathrm{d}[\mathrm{NaRFe(CO)_4}]}{\mathrm{d}t} = k_2(\text{obsd})[\mathrm{Na_2Fe(CO)_4}]_{\text{total}}[\mathrm{RX}] \tag{4}$$

Where eq 12 in eq 5 yields:

$$k_2(\text{obsd}) = [(k_{2-} - k_{2\pm})(K_{1D})^{1/2}] \times \frac{1}{[\mathrm{Na_2Fe(CO)_4}]^{1/2}{}_{\text{total}}} + k_{2\pm} \tag{13}$$

References and Notes

(1) For reviews of the oxidative-addition reaction see (a) J. P. Collman, *Acc. Chem. Res.*, 1, 136 (1968); (b) J. P. Collman and W. R. Roper, *Adv. Organomet. Chem.*, 7, 53 (1968); (c) J. Halpern, *Acc. Chem. Res.*, **3**, 386 (1968); (d) J. A. Osborn in "Organotransition-Metal Chemistry", Y. Ishii and M. Tsutsui, Ed., Plenum Press, New York, N.Y., 1975, pp 65–80. For closely related reviews see also: (e) R. Cramer, *Acc. Chem. Res.*, 1, 186 (1968); (f) L. Vaska, *ibid.*, 1, 335 (1968); (g) G. W. Parshall, *ibid.*, **3**, 139 (1970).

(2) We shall restrict our discussion to alkyl halide addenda.

(3) P. W. Schneider, P. F. Phelan, and J. Halpern, *J. Am. Chem. Soc.*, **91**, 77 (1969); J. Halpern and J. P. Maher, *ibid.*, **87**, 5361 (1965); J. Kwiatek and J. K. Seyler, *J. Organomet. Chem.*, **3**, 421 (1965).

(4) J. S. Bradley, O. E. Connors, D. Dolphin, J. A. Labinger, J. A. Osborn, *J. Am. Chem. Soc.*, **94**, 4043 (1972); J. A. Labinger, A. V. Kramer, and J. A. Osborn, *ibid.*, **95**, 7908 (1973).

(5) (a) J. P. Collman and M. R. MacLaury, *J. Am. Chem. Soc.*, **96**, 3019 (1974); (b) M. MacLaury, Ph.D. Thesis, Stanford University, Stanford, Calif., 1974; (c) P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, **88**, 3511 (1966); (d) G. N. Schrauzer and E. Deutsch, *ibid.*, **91**, 3341 (1969).

(6) J. A. Labinger, R. J. Braus, D. Dolphin, and J. A. Osborn, *Chem. Commun.*, 612 (1970); F. R. Jensen and B. Knickel, *J. Am. Chem. Soc.*, **93**, 6339 (1971); R. G. Pearson and W. R. Muir, *ibid.*, **92**, 5519 (1970).

(7) C. D. Cooke and G. S. Jauhal, *Can. J. Chem.*, **45**, 301 (1967); R. Ugo, *Coord. Chem. Rev.*, **3**, 319 (1968); J. P. Birk, J. Halpern, and A. L. Pickard, *Inorg. Chem.*, 7, 2672 (1968); J. P. Birk, J. Halpern, and A. L. Pickard, *J. Am. Chem. Soc.*, **90**, 4491 (1968).

(8) (a) A. V. Kramer, J. A. Labinger, J. S. Bradley, and J. A. Osborn, *J. Am. Chem. Soc.*, **96**, 7145 (1974); (b) A. V. Kramer and J. A. Osborn, *ibid.*, **96**, 7832 (1974); (c) I. H. Elson, D. G. Morrell, and J. K. Kochi, *J. Organomet. Chem.*, **84**, C7 (1975); (d) K. S. Y. Lau, R. W. Fries, and J. K. Stille, *J. Am. Chem. Soc.*, **96**, 4983 (1974); (e) K. S. Y. Lau, P. W. Wong, and J. K. Stille, *ibid.*, **98**, 5832 (1976); J. K. Stille and K. S. Y. Lau, *ibid.*, **98**, 5841 (1976).

(9) (a) M. P. Cooke, *J. Am. Chem. Soc.*, **92**, 6080 (1970); (b) J. P. Collman, S. R. Winter, and D. R. Clark, *ibid.*, **94**, 1788 (1972); (c) J. P. Collman, S. R. Winter, and R. G. Komoto, *ibid.*, **95**, 249 (1973).

(10) J. P. Collman, *Acc. Chem. Res.*, **8**, 342 (1975).

(11) J. P. Collman, J. N. Cawse, and J. I. Brauman, *J. Am. Chem. Soc.*, **94**, 5905 (1972).

(12) (a) M. Szwarc, "Ions and Ion Pairs in Organic Reactions", Vol. II, Wiley, New York, N.Y., 1974. The effect of ion-pairing upon the kinetics of oxidative-additions to $\mathrm{Na_2Fe(CO)_4}$ is analogous to other systems where free anions are more reactive than ion-pairs. The best studied such system is the anionic polymerization of styrene, Chapter 4, Vol. II; (b) *ibid.*, p 385.

(13) The following abbreviations are used in this paper: THF = tetrahydrofuran, NMP = *N*-methylpyrrolidinone, $\mathrm{PPN^+}$ = bis(triphenylphosphine)iminium cation, DMDI = 1,4-diaza-1,4-dimethylbicyclo[2.2.2]octane diiodide, HMPA = hexamethylphosphorictriamide.

(14) W. O. Siegl and J. P. Collman, *J. Am. Chem. Soc.*, **94**, 2516 (1972).

(15) G. Huttner and W. Gartztk, *Chem. Ber.*, **108**, 1373 (1975).

(16) S. R. Winter, Ph.D. Thesis, Stanford University, Stanford, Calif., 1973.

(17) J. R. Shapley and J. A. Osborn, *Acc. Chem. Res.*, **6**, 305 (1973), and references therein. J. P. Jesson and E. L. Muetterties in "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975, pp 266–277.

(18) The decomposition is accelerated above 0 °C and in more concentrated solutions. Attempts to isolate anionic $\mathrm{RFe(CO)_4^-}$ decomposition product(s) as $\mathrm{PPN^+}$ salts gave only small amounts of $\mathrm{(PPN)_2Fe_2(CO)_8}$ and $\mathrm{(PPN)_2Fe_3(CO)_{11}}$, the fate of the alkyl remaining unknown. The presence of triple-ions[10] such as $\mathrm{(RFe(CO)_4^-{:}Na^+{:}RFe(CO)_4)^-}$ in more concentrated solutions may provide a disproportionation decomposition pathway to relatively stable binuclear products.[19]

(19) Stable binuclear bridging oxycarbene iron compounds such as $\mathrm{(CO)_3Fe{-}Fe(COR)_2(CO)_3}$ are known. P. F. Lindley and O. S. Mills, *J. Chem. Soc. A*, 1279 (1969); D. St. P. Bunbury, E. Frank, P. F. Lindley, O. S. Mills, E. O. Fischer, and V. Kiener, *Chem. Commun.*, 1378 (1968).

(20) R. W. Alder, R. Baker, and J. M. Brown, "Mechanism in Organic Chemistry", Wiley, New York, N.Y., 1971, pp 85–92.

(21) (a) W. F. Edgell in "Ions and Ion Pairs in Organic Reactions", Vol. I, M. Szwarc, Ed., Wiley, New York, N.Y., 1972, pp 153–176; (b) *ibid.*, p 165; (c) W. F. Edgell and N. Pauuwe, *Chem. Commun.*, 284 (1969). (d) After a preliminary report of this work appeared,[10] Darensbourg[21e] published a report describing ion-pair interactions between alkali metal cations and manganese carbonyl anions. Consistent with our studies[11,21f,57] in THF of the metal carbonyl monoanions $\mathrm{RFe(CO)_4^-}$, $\mathrm{RC({=}O)Fe(CO)_4^-}$, and $\mathrm{HFe_2(CO)_8^-}$, their IR and conductivity studies demonstrate that the addition of cation solvating agents as 15-crown-5-crown ether or HMPA generate predominantly solvent-separated ion-pairs. They have examined the reaction of $\mathrm{Mn(CO)_5^-}$ with activated alkyl halides (e.g., $\mathrm{PhCH_2Cl}$). Interestingly, the addition of crown ethers or HMPA to $\mathrm{NaMn(CO)_5}$ in THF *de*creases the rate of this reaction, a result exactly opposite that found in our study of $\mathrm{Na_2Fe(CO)_4}$. Their system is complicated by the presence of triple ions and higher ion aggregates which are not formed by $\mathrm{Na_2Fe(CO)_4}$ in THF or NMP. These ion aggregates complicate the interpretation of conductivity, IR, and kinetic results. For example, the rate constants are composite values of unknown contributions by ion-pairs, triple-ions, higher ion-aggregates, and their (pre) equilibrium constants. Furthermore, the activation parameters are also composite values. (e) M. Y. Darensbourg, D. J. Darensbourg, D. Burns, and D. A. Drew, *J. Am. Chem. Soc.*, **98**, 3127 (1976); (f) J. P. Collman, R. G. Finke, J. N. Cawse, and J. I. Brauman, submitted for publication.

(22) J. M. Lehn, *Struct. Bonding* (*Berlin*), **16**, 1 (1973).

(23) Kryptofix 222 is the trade name for 4,7,13,16,21,24-hexaoxy-1,10-diazabicyclo[8.8.8]hexacosane, and can be purchased from E. M. Laboratories, Inc.

(24) In $\mathrm{H_2O}$, the $\mathrm{Na^+}$ binding constant[22] is $10^{3.9}$.

(25) (a) To a first approximation, assuming mobility is independent of concentration, $\alpha = \Lambda/\Lambda_0$, but from the conductometric titration $\Lambda_0 = \Lambda_f$ where $\Lambda_f = k_F/[\mathrm{Na_2Fe(CO)_4}]_{\text{total}}\cdot$(mobility correction) (Figure 1). This mobility correction arises from the different size and thus different mobility of $\mathrm{Na^+}$ vs. (cryptate·$\mathrm{Na^+}$) in NMP (and not the mobility's concentration dependence). Using $\mathrm{NaBPh_4}$ in NMP as a model, with and without 1 equiv of cryptand, the mobility correction = $\Lambda(\mathrm{NaBPh_4})/\Lambda\cdot(\text{cryptate}\cdot\mathrm{NaBPh_4})$ = 1.113. Thus $\alpha = \Lambda 1.113)/(\Lambda_F) = k1.113/k_F = 0.793$, and $K_D = [\mathrm{Na_2Fe(CO)_4}]_{\text{total}}\alpha^2/(1-\alpha) = 0.28$ M. Since rigorously[26] $\Lambda_F < \Lambda_0$, $K_D < 0.28$ M one could obtain Λ_0 precisely from the concentration dependence of $\mathrm{(cryptate{\cdot}Na)^+NaFe(CO)_4^-}$, $\mathrm{(cryptate{\cdot}Na)^+BPh_4^-}$, and $\mathrm{NaBPh_4}$, and using the Onsager equation, $\Lambda = \Lambda_0 - ac^{1/2}$, where a = constant, c = concentration. However, the $\mathrm{H_2O}$ sensitivity of $\mathrm{Na_2Fe(CO)_4}$ precluded such an experiment. (b) If triple ions were formed by $\mathrm{Na_2Fe(CO)_4}$ in NMP, k_1 (Figure 1) and thus the calculated[25a] K_{1D} would be too large and would not agree with the value determined independently[32] using kinetics. A consideration of the Λ value for $\mathrm{Na_2Fe(CO)_4}$ in NMP plus 2 or more equiv of cryptate proves that these conditions yield free $\mathrm{Fe(CO)_4^{2-}}$. Since this value, Λ ($\mathrm{Na_2Fe(CO)_4}$ + 2cryptate) = $2.9 \times 10^{-2}\ \Omega^{-1}$/M, is the same within experimental error as that calculated using Kohlrausch's law for $\mathrm{2Na^+ + Fe(CO)_4^{2-}}$, $\Lambda_0(\text{calcd}) = [2\lambda_0{}^+(\mathrm{Na^+}) + \tfrac{1}{2}\lambda_0{}^{2-}(\mathrm{Fe(CO)_4^{2-}})] = 3.0 \times 10^{-2}\ \Omega^{-1}$/M, free $\mathrm{Fe(CO)_4^{2-}}$ must be formed. The experimental value for Λ_0 ($\mathrm{Na^+}$·cryptate + $\mathrm{NaFe(CO)_4^-}$) $\simeq \Lambda_F$ ($\equiv k_F/[\mathrm{Na_2FeCO)_4}]$, Figure 1), the reasonable approximations $\lambda_0{}^+(\mathrm{Na^+}\cdot\text{cryptate}) \simeq \lambda_0{}^-(\mathrm{NaFe(CO)_4^-})$ and $\lambda_0{}^-(\mathrm{NaFe(CO)_4^-}) \simeq \tfrac{1}{2}\lambda_0{}^{2-}(\mathrm{Fe(CO)_4^{2-}})$ and Kohlrausch's law were used to calculate approximate values for $\lambda_0{}^+(\mathrm{Na^+})$ and $\tfrac{1}{2}\lambda_0{}^{2-}(\mathrm{Fe(CO)_4^{2-}})$.

(26) For systems like $\mathrm{Na_2Fe(CO)_4}$ in NMP or THF that do not form triple ions or higher aggregates the equivalent conductance, Λ, always decreases with increasing concentration (see Figure 3). R. M. Fuoss, *Proc. Natl. Acad. Sci. U.S.A.*, 71, 4491 (1974).

(27) The first sharp breakpoint requires $K_{1O} \gtrsim 10^2K_{2O}$. The second sharp breakpoint with the zero slope observed after 2 equiv of cryptand/$\mathrm{Na_2Fe(CO)_4}$ requires $K_{2O} \gtrsim 10^2K_D$ (cryptate·$\mathrm{Na^+}$). Although the binding constant of $\mathrm{Na^+}$ by Kryptofix 222 in NMP is not known exactly, by examining solvent effects on crown ether $\mathrm{Na^+}$ complexation constants[28] one finds that:

$$K_D(\mathrm{H_2O}) \gtrsim K_D(\text{dipolar aprotic}) > 10K_O(\mathrm{MeOH})$$

In general, for cryptands, $K_D(H_2O) \times 10^4 \simeq K_D(MeOH)$,[22] and for Kryptofix 222, $K_D(H_2O) = 10^{-3.9}$ M, $K_D(MeOH) < 10^{-8}$ M. Thus we have: $10^{-3.9}$ M $> K_O(NMP) > 10^1 \cdot 10^{-3.9}$ M; $10^{-2} \cdot 0.2$ M $> K_{2D} > 10^2 \cdot K_D(NMP)$; 10^{-3} M $> K_{2O} > 10^{-5}$ M.

(28) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 373 (1974). The Na^+ complexation constants for the B isomer of dicyclohexyl-18-crown-6 in H_2O, Me_2SO, and MeOH are $10^{1.2-1.6}$, $10^{1.7}$, and $10^{3.7}$, respectively. For the A isomer in H_2O and MeOH they are $10^{1.5-1.8}$ and $10^{4.1}$, respectively.

(29) (a) R. M. Fuoss and F. Accascina, "Electrolytic Conductance", Interscience, New York, N.Y., 1959, p 4. This equation is valid only for weak electrolytes at low concentration. (b) *ibid.*, p 92.

(30) The slope and intercept of an Ostwald plot are 2.2×10^7 M/$(\Omega^{-1})^2$ and -5.1×10^1 M/Ω^{-1}. However, the H_2O sensitivity of $Na_2Fe(CO)_4$ and the fact that Λ_0 is large, both make the intercept of an Ostwald plot, $1/\Lambda_0$, unreliable. The value[25] $\Lambda_0(NMP) \simeq \Lambda_F$(mobility correction) $= 2.4 \times 10^{-2}\ \Omega^{-1}$/M and the Walden product rule, $\eta\Lambda_0(NMP) = \eta\Lambda_0(THF)$ have been used to obtain $\Lambda_0(THF) \simeq 9.5 \times 10^{-2}\ \Omega^{-1}$/M, which, when combined with the slope of the Ostwald plot, give $K_O \simeq 5 \times 10^{-8}$ M. The validity of $\Lambda_0 \simeq 9.5 \times 10^{-2}\ \Omega^{-1}$/M for $Na_2Fe(CO)_4$ in THF is supported by the known values $\Lambda_0 = 11.0 \times 10^{-2}\ \Omega^{-1}$/M[21b] and $\Lambda_0 = 8.8 \times 10^{-2}\ \Omega^{-1}$/M[43] for $NaCo(CO)_4$ and $NaBPh_4$ in THF, respectively.

(31) R. M. Fuoss in "Computer Programs for Chemistry", Vol. 5, K. B. Wiberg, Ed., Academic Press, New York, N.Y., in press. We were advised that our system did not meet the requirements necessary for the use of this program (R. M. Fuoss private communication).

(32) From eq 5 and 7, Appendix I, we see that, after truncation of terms higher than second order

$$k_2(\text{obsd}) = a + b[Na_2Fe(CO)_4]_T + c[Na_2Fe(CO)_4]_T^2$$

$a = k_{2-}$, $b = -(k_{2-} - k_{2\pm})/K_{1O}$, $c = 2(k_{2-} - k_{2\pm})/(K_{1O})^2$. Constraining $k_{2\pm} = 0$, a second-order least-squares polynomial fit for k_2(obsd) as a function of $[Na_2Fe(CO)_4]$ gives $a = 0.184 \pm 0.003$, $b = -0.74 \pm 0.01$, $c = 2.42 \pm 0.81$, which give $k_{2-} = 0.184 \pm 0.003\ M^{-1}\ s^{-1}$, $K_{1D} = 0.24 \pm 0.04$ M, and $K_{1O} = 0.39 \pm 0.22$. The error bars represent one standard deviation. Note that the primary salt effect, which should be negligible for an ion $([Na^+{:}S{:}Fe(CO)_4^{2-}])^-$ reacting with a neutral molecule (RX), as well as the secondary salt effect upon the dissociative equilibria have not been included, since activity coefficients have been neglected. The dependence of k_2(obsd) with $[Na_2Fe(CO)_4]$ cannot be studied at constant ionic strength, since added salts are not inert (e.g., Bu_4NBPh_4, Figure 5) but have a large ion-pairing effect. However, K_{1O} should still be accurate to at least one significant figure, $K_{1O} = 0.2 \pm 0.1$.

(33) G. R. Stevenson and A. E. Alegria, *J. Am. Chem. Soc.*, **97**, 3869 (1975).

(34) If free $Fe(CO)_4^{2-}$ were the kinetically dominant species in NMP, a rate decrease of at least 40-fold should have been seen.

(35) Ion-pair reactivities show a marked solvent dependence. For the anionic polymerization of styrene[12] in good cation solvating solvents, the ion-pair reactivities are $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ with the order reversed in poor cation solvating solvents such as dioxane.

(36) G. N. Schrauzer and E. Deutsch, *J. Am. Chem. Soc.*, **91**, 3341 (1969).

(37) R. G. Pearson, H. Sobel, and J. Songstad, *J. Am. Chem. Soc.*, **90**, 319 (1968).

(38) (a) If we instead use the measured rate in THF of *n*-RI and multiply by the observed NMP to THF rate increase and by the methyl vs. *n*-alkyl ratio, again $n = 16.8$. (b) The chloride vs. iodide ratio was measured in THF. (c) The value $n = 15.2$ was estimated from the rate of reaction of $CpFe(CO)_2^-$ with EtBr in glyme, $k_2 = 139\ M^{-1}\ s^{-1}$. R. E. Dessey, R. L. Dohl, and R. B. King, *J. Am. Chem. Soc.*, **88**, 5121 (1966).

(39) A. Streitwieser, Jr., "Solvolytic Displacement Reactions", McGraw-Hill, New York, N.Y., 1962, p 13.

(40) For example, 4 equiv of $H_2O/Na_2Fe(CO)_4$ decrease the rate of RBr oxidative-addition ≃ fivefold and the yield ≃40% (entry no. 4, Table III). In a reaction in THF with 2 equiv of $H_2O/Na_2Fe(CO)_4$, 11% $HFe(CO)_4^-$ (based on $Na_2Fe(CO)_4$) was isolated as its PPN^+ salt and identified by IR and NMR.

(41) The observed 5×10^4 increase in K_{1O} in NMP vs. THF can account for only a 10^2 increase in the degree of dissociation, α, at 0.10 M $Na_2Fe(CO)_4$ and thus only a 10^2 rate increase. At 0.01 M $Na_2Fe(CO)_4$, the increase in K_{1O} can account for only a 40-fold rate increase.

(42) For the anionic polymerization of styrene, the rate constants of the free ions, k_{2-}, never deviate from their average value by more than a factor of 2, whatever the solvent.[12b]

(43) J. Smid and M. Szwarc, *J. Phys. Chem.*, **69**, 608 (1965).

(44) We are unaware of alkyl tosylates reacting via these one-electron mechanisms.

(45) Other oxidative-additions that go by inversion at carbon include: (a) P. K. Wong, K. S. Y. Lau, and J. K. Stille, *J. Am. Chem. Soc.*, **96**, 3956 (1974), and references therein; (b) G. M. Whitesides and D. J. Boschetto, *ibid.*, **91**, 4313 (1969).

(46) For an excellent discussion of the stereochemistry of reactions at carbon–transition metal bonds see P. L. Bock, D. J. Boschetto, J. R. Rasmussen, J. P. Demers, and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 2814 (1974).

(47) Since k_2(obsd) is proportional to $K_D^{1/2}$ in THF (eq 13, Appendix I), the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are composite values and include a contribution from the ion-pairing equilibrium.

(48) M. H. R. Hoffman, *J. Chem. Soc.*, 6753 (1965).

(49) C. H. Depuy and C. A. Bishop, *J. Am. Chem. Soc.*, **82**, 2532 (1960).

(50) S. Winstein, E. C. Friedrich, and S. Smith, *J. Am. Chem. Soc.*, **86**, 305 (1964).

(51) C. L. Perrin and J. Pressing, *J. Am. Chem. Soc.*, **93**, 5705 (1971), and references contained therein. Perrin and Pressing have offered a simple statistical mechanical model based on dipole–dipole interactions between the salt and the reactants in its transition state to account for linear "normal" salt effects.

(52) R. G. Komoto, Ph.D. Thesis, Stanford University, Stanford, Calif., 1974.

(53) Commercially available from Alfa Ventron.

(54) D. M. Adams, "Metal-Ligand and Related Vibrations", St. Martin's Press, New York, N.Y., 1968, p 84.

(55) R. G. Teller, R. G. Finke, J. P. Collman, H. B. Chin, and R. Bau, *J. Am. Chem. Soc.*, **99**, 1104 (1977).

(56) R. Bau and H. B. Chin, *J. Am. Chem. Soc.*, **98**, 2434 (1976).

(57) J. P. Collman, R. G. Finke, P. L. Matlock, and J. I. Brauman, *J. Am. Chem. Soc.*, **98**, 4685 (1976).

(58) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.

(59) C. H. DePuy, G. F. Morris, J. S. Smith, and R. J. Smat, *J. Am. Chem. Soc.*, **87**, 2421 (1965).

(60) R. M. Izatt, B. L. Haymore, J. S. Bradshaw, and J. J. Christensen, *Inorg. Chem.*, 14, 3132 (1975).

(61) D. P. Shoemaker and C. W. Garland, "Experiments in Physical Chemistry", McGraw-Hill, New York, N.Y., p 136.

(62) P. R. Bevington, "Data Reduction and Error Analysis for the Physical Sciences", McGraw-Hill, New York, N.Y., 1969, Chapter 8.