

can only mean that the Franck-Condon factors for the vibrational wavefunctions, the latter two integrals, in the lowest energy transitions must be significantly larger than those associated with the higher energy transitions. Therefore the true configuration must be consistent with this observation.

Conclusion

We have investigated two polymorphic forms of $K_2[Ni(dto)_2]$ using IR and RR spectroscopy. Through the use of metal-isotope substitution and normal coordinate treatment, definitive assignments of vibrational frequencies have been made for the red form of the complex. These assignments have allowed us to detect small changes in bond lengths within the first coordination sphere of the Ni complexes which were not evident in the X-ray data.

Resonance Raman excitation profiles of the red form of the complex clearly defined the three electronic transitions proposed earlier by Latham et al.⁶ Furthermore, the unusual nature of the excitation profiles of the red complex places a useful restriction on the order of the highest occupied molecular orbitals. Finally, overtone sequences of the fundamental ν_1 mode and a combination mode involving ν_1 of the red complex have allowed us to calculate the anharmonicity constant for ν_1 .

Acknowledgment. This work was partly supported by the National Science Foundation (CHE-7915169). We wish to express our sincere thanks to Professor D. F. Shriver of Northwestern University who kindly measured the far-infrared spectra of the title compounds.

Interactions of $CpM'(CO)_3^-$ ($M' = Cr, Mo, W$) with Cations: Effects on CO Exchange and RX Addition Reactions

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Abstract: Solution structures of Li^+ , Na^+ , K^+ , Me_4N^+ , PPN^+ , and $M^+(HMPA)_x$ salts of $CpM'(CO)_3^-$ ($M' = Cr, Mo, W$) in tetrahydrofuran have been defined by analysis of their $\nu(CO)$ IR spectra. Interaction of alkali cations with one carbonyl oxygen is apparent. For the large bis(triphenylphosphine)iminium and HMPA solvated cations, which conductivity measurements showed to exist as associated ion pairs in THF, a non-cation-perturbed, C_{3v} , $CpM'(CO)_3^-$ ion structure exists in solution. The Me_4N^+ cation strongly interacts with the carbonylates; however, the symmetry of the perturbed $CpM'(CO)_3^-$ could not be established. Small amounts (ca. 20 equiv) of the good alkali cation complexing agent HMPA were required to solvent-separate ion pairs of $M^+CpM'(CO)_3^-$ in THF, whereas 400 equiv of CH_3CN was required to achieve a similar environment for the $CpM'(CO)_3^-$. Force constant calculations showed that Li^+ caused the greatest reorganization of electron density in the contact ion paired $CpMo^-(CO)_2(CO \cdots Li^+)$ as contrasted to symmetrically solvated $CpMo(CO)_3^-$; however, the lifetime of such ion-pair interactions is short on the NMR time scale as shown by both C-13 and O-17 NMR studies. Carbon-13 labeled CO exchange into $CpMo(CO)_3^-$ was found to be counterion dependent with rates decreasing as $Li^+ > Na^+ > PPN^+$. The presumed intermediate, coordinatively unsaturated $[CpMo(CO)_2^-]$, was readily scavenged by ^{13}CO but not by phosphine ligands. The nonactivated RX molecules *n*-BuI and *n*-BuBr were found to undergo halide displacement by symmetrically solvated $CpMo(CO)_3^-$, in typical S_N2 fashion, more rapidly than with the contact ion pairs $CpMo^-(CO)_2Co \cdots Na^+$. For $RX = BzCl$, the opposite counterion effect was observed. Finding no evidence for radical intermediates, a cation-assisted transition-state formation was asserted for the reaction $Na^+CpMo(CO)_3^- + BzCl \rightarrow CpMo(CO)_3BzCl$.

Introduction

Over the past 10 years a considerable body of knowledge has accrued regarding the solution structures of highly reactive and important transition metal carbonylates. In a classic group of experiments, the use of $Co(CO)_4^-$ as a probe of solution environment about alkali cations evolved into a rigorous study of the sites of carbonylate ion pairing in various solvents.^{1,2} Others have been concerned with the redistribution of electronic charge in the carbonylate itself upon changing the electrostatic potential of the counterions,³⁻⁸ or to ion-pair site specificity in nonsymmetric carbonylates.^{3,5,6} The ability of $\nu(CO)$ infrared spectroscopy to detect very small structural and electronic changes as well as the availability of a substantial arsenal of appropriate solid-state structural studies of metal carbonylates has promoted the development of a new subdiscipline in ion-pairing phenomena.

The reactivity of transition metal carbonylates is of import to both organic⁹ and organometallic¹⁰ synthesis and to catalysis. Early studies established a nucleophilicity scale which had its experimental origins in kinetic studies of the reaction of carbonylates with alkyl halides, monitored by electrochemical methods.¹¹

The rate expression was $rate = k_2[M^+CO^-][RX]$, and a relative comparison of second-order rate constants was set forth as the nucleophilicity scale: $CpFe(CO)_2^- (7 \times 10^7) > CpNi(CO)_2^- (5.5 \times 10^6) > CpW(CO)_3^- (550) > Mn(CO)_5^- (77) > CpMo(CO)_3^- (67) > CpCr(CO)_3^- (4) > Co(CO)_4^- (1, reference)$.¹¹ The nucleophilicity scale has quite possibly been used to correlate more data than any other physical organometallic study carried out to date.

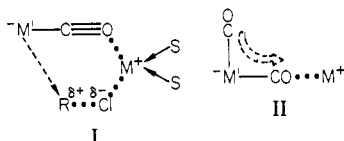
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The typical mode of preparation of transition metal carbonylates for synthetic or mechanism study purposes is by direct metal, metal amalgam, or metal hydride reductions in a solvent of low polarity and donor ability, tetrahydrofuran (THF; dielectric constant $D = 7.4$). Extensive alkali or alkaline earth cation/carbonylate anion interactions are common in these systems. Prior to this study detailed analyses of THF-solution $\nu(\text{CO})$ IR and adjunct data established sites and extent of alkali cation interaction with the following members of the original nucleophilicity scale: $\text{CpFe}(\text{CO})_2^-$,^{7,8} $\text{Mn}(\text{CO})_5^-$,^{3,4} and $\text{Co}(\text{CO})_4^-$,^{1,2} as well as $\text{LV}(\text{CO})_5^-$.⁶ We have extended the account of ion pairing by studying the propensity of $\text{CpM}'(\text{CO})_3^-$ ($\text{M}' = \text{Cr}, \text{Mo}, \text{W}$) to form contact ion pairs as a function of cation (Li^+ , Na^+ , K^+ , Me_4N^+ , $[\text{Ph}_3\text{PNPPH}_3]^+$ (PPN^+)) and solvent (Et_2O , $\text{Et}_2\text{O}/\text{HMPA}$, THF, THF/HMPA, and CH_3CN), and report herein.

Since the nucleophilicity scale was determined under conditions of little perturbing cation/carbonylate anion interaction, questions regarding the generality of the scale arise in cases where structural and electronic modifications of the carbonylate exist owing to contact ion pairing. It has been shown that in some cases contact ion-pair structures of carbonylates participate in nucleophilic addition reactions with more facility than does the carbonylate when freed from the perturbation and charge-neutralizing capabilities of the alkali cation. These include the ring-opening reaction of epoxides by $\text{M}^+\text{CpFe}(\text{CO})_2^-$,⁸ the addition of benzyl- and substituted benzyl chlorides to $\text{M}^+\text{Co}(\text{CO})_4^-$,¹² the addition of benzyl chloride and allyl chloride to $\text{LMn}(\text{CO})_4^-$ ($\text{L} = \text{CO}, \text{PR}_3, \text{P}(\text{OR})_3$),³ and the addition of benzyl chloride to $\text{CpMo}(\text{CO})_3^-$.¹³ The last study established that the rate enhancement by contact ion pairs as opposed to solvent-separated ion pairs occurred for benzyl chloride whereas reactions with alkyl halides such as *n*-butyl bromide or iodide showed the opposite (and more traditional) counterion effect; i.e., rates of reaction were accelerated as the anionic charge of the nucleophile was made more available owing to the separation of contact ion pairs. The reports on the benzylic chloride reactions all stressed the importance of a highly ordered transition state (I) in which cation assist $\text{R}^{\delta+}\cdots\text{C}|\delta-$ bond



cleavage is essential to the lowered barrier to reaction. A more complete report of our study¹³ of nucleophilic addition reactions of $\text{CpMo}(\text{CO})_3^-$ is presented below.

Structure II indicates the electronic drift toward the cation interacting site of a metal carbonylate which might influence a different general reaction. Interpretation of $\nu(\text{CO})$ IR spectra suggest that the CO bond order is significantly reduced in the group $\text{M}'\text{-CO}\cdots\text{M}^+$ and increased in the noncation interacting $\text{M}'\text{-CO}$ as compared to a metal carbonylate in a symmetrical solvent environment. Making the successful Cotton/Wing¹⁴ assumption that $\text{M}'\text{-C}$ bond orders vary oppositely to CO bond orders, it is expected that $\text{M}'\text{-CO}$ bond cleavage reactions should be facilitated in solutions where contact ion pairing is prevalent. The CO exchange reaction of $\text{CpMo}(\text{CO})_3^-$ with ^{13}CO proceeds conveniently, and a study of its rate as a function of counterion is also presented.

Experimental Section

A. Materials. 1. **Solvents.** Tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), and benzene were distilled from the purple Na^0 /benzophenone scavenger, collected, and transferred under nitrogen. Acetonitrile was stirred over CaH_2 , decanted, distilled from P_2O_5 , and degassed by three freeze-thaw cycles prior to use. Hexane was stirred over concentrated H_2SO_4 , washed with aqueous bicarbonate and distilled

water, and then stored over and distilled from CaSO_4 under N_2 . Freeze-thaw degassing preceded use. Hexamethylphosphoric triamide (HMPA) was distilled under vacuum; the first and last 10% of distillate were discarded.

2. Reagents. Common reagents were purchased from ordinary vendors and used as received. Carbon-13 labeled CO gas (93.3% ^{13}CO) was obtained from Prochem, B.O.C. Ltd., London. 1,4-Cyclohexadiene was dried over CaSO_4 and distilled in vacuo. Normal butyl iodide, bromide, and chloride, benzyl chloride, and $\text{P}(\text{OPh})_3$ were distilled from P_2O_5 under partial vacuum. The first and last 10% fractions of distillates were discarded. Three freeze-thaw cycles were applied and the liquids stored under argon in the dark in flasks fitted with wired-on rubber septa. These reagents and HMPA were stored for a maximum of 2 weeks. *Caution:* HMPA is a potent carcinogen.

B. Instrumentation. Infrared spectra were recorded on either a Perkin-Elmer 521 or a 283B spectrophotometer. Spectra were calibrated with molybdenum hexacarbonyl (1989.1 cm^{-1} in hexane) as standard. A Varian-3 electron spin resonance spectrophotometer was also used during the course of these experiments. Carbon-13 NMR spectra were recorded on a JEOL FX60 at Tulane University, and oxygen-17 NMR spectra were taken on a Varian XL-100-15 operating at 13.57 MHz at the University of Indiana.

C. Methods. An inert-atmosphere glovebox and Schlenk and/or high-vacuum techniques were used to render all transfers and sample preparations air and moisture free.

1. Preparation of $\text{M}^+\text{CpM}'(\text{CO})_3^-$. The $[\text{CpM}'(\text{CO})_3]_2$ used as precursors to the anions were prepared according to published procedures.¹⁵ A small light glass rod which extended into the reflux condenser and which was agitated by the magnetic stir bar served to prevent buildup of the volatile $\text{M}(\text{CO})_6$ in the reflux condenser. The reduction of the dimers was via alkali metal/Hg amalgam and a typical preparation follows. A 0.004-mol sample of $[\text{CpMo}(\text{CO})_3]_2$ was dissolved in 50 mL of degassed THF. This solution was then transferred via cannula into an air-free round-bottom flask containing a previously prepared amalgam (0.008 mol of Na/4 mL of Hg). The mixture was stirred at room temperature until the red-violet color of the dimer turned to a grayish-green (~ 45 min). The supernatant was transferred via cannula into a septum-capped, degassed centrifuge tube. Centrifugation was necessary since the fine powder produced by the amalgam hindered direct filtration. After centrifugation the supernatant was filtered using an airless fritted apparatus. The solvent was then evaporated under vacuum and the yellowish residue recrystallized from THF/benzene. The resulting solid was an air-sensitive yellowish powder. The yield after recrystallization was approximately 90%. The lithium salt is known to crystallize with a molecule of THF in its lattice;¹⁶ consequently, solvent removal was achieved by evacuating the heated ($\sim 80^\circ\text{C}$) solid.

2. Preparation of Bis(triphenylphosphine)iminium Cyclopentadienylmolybdenum Tricarbonyl. A 10-mL portion of THF containing 1.58 mmol of $\text{NaCpMo}(\text{CO})_3$ was mixed with a solution of PPNCl (1.59 mmol) in 4 mL of dichloromethane. The mixture was stirred and subsequently filtered. Hexane was added to precipitate the product which was obtained in 90% yield on filtration. The yellow powder was recrystallized from a 5:1 mixture of THF/ CH_2Cl_2 with hexane as precipitating agent.

3. Preparation of $\text{CpMo}(\text{CO})_3\text{CH}_2\text{Ph}$. A 5-mL solution of 1.87 mmol of $\text{Na}^+\text{CpMo}(\text{CO})_3^-$ and 1.87 mmol of BzI in THF was allowed to react for 3 h in a centrifuge tube. The white solid (NaBr) formed was separated by centrifugation and the supernatant was transferred into a Schlenk flask. After solvent removal an intense-yellow residue remained. This solid was dissolved in a minimal amount of hexane by heating lightly and then allowed to sit overnight. The clusters of air-stable yellow needles obtained were filtered and dried under vacuum to give an isolated 70% yield. Anal. (Galbraith Laboratories, Knoxville, Tenn.). Calcd for $\text{C}_{15}\text{H}_{12}\text{MoO}_3$: C, 53.59; H, 3.60. Found: C, 53.35; H, 3.60. The proton NMR spectrum in CD_3CN showed a multiplet at 7.17 ppm and singlets at 5.32 and 2.89 ppm of relative intensities 5:5:2 assigned to the phenyl, cyclopentadienyl, and methylene protons, respectively. The $\nu(\text{CO})$ infrared showed a sharp medium absorbance at 2007 cm^{-1} and a strong, relatively broad absorbance at 1927 cm^{-1} in THF solution.

4. Preparation of ^{13}CO -Enriched Carbonylates and Kinetics of Ligand Exchange. Carbon-13 enrichment of $\text{CpMo}(\text{CO})_3^-$ was achieved by adding ^{13}CO to a 100-mL evacuated flask containing 5 mL of a 0.029 M solution of $\text{M}^+\text{CpMo}(\text{CO})_3^-$ and a stir bar. The approximate rate of exchange was obtained by an IR monitor of withdrawn samples. The

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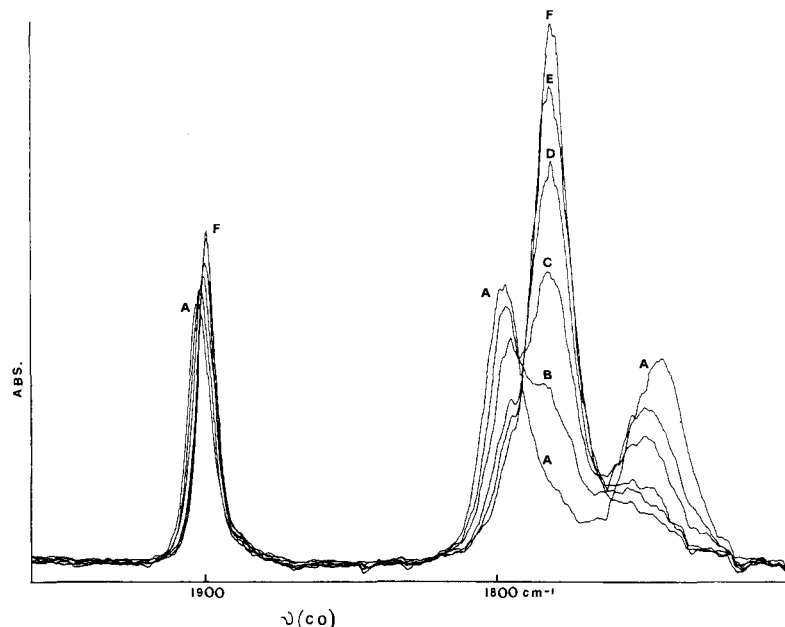


Figure 1. $\nu(\text{CO})$ IR spectra of $\text{Na}^+\text{CpMo}(\text{CO})_3^-$ in THF (0.03 M) as a function of incremental addition of HMPA. A = pure THF, B = 2 HMPA/ Na^+ , C = 4 HMPA/ Na^+ , D = 7 HMPA/ Na^+ , E = 9 HMPA/ Na^+ (1.2% (v/v) HMPA/THF), F = pure HMPA.

concentration of ^{13}CO in the reaction flask was varied by adding ^{13}CO to the evacuated flask using, when necessary, Ar to bring the total pressure to 1 atm. Spectra for precise frequency data and for publication were taken on solutions which were allowed to react for a period of time, degassed, backfilled with Ar and samples taken of the partially completed exchange reaction. A computer average (via the Perkin-Elmer data station) of four scans per spectrum and computer subtraction of a background scan aided in smoothing the spectra.

Attempts to exchange the carbonyl ligands for PPh_3 or $\text{P}(\text{O}i\text{Pr})_3$ consisted of adding a 20-fold excess of ligand to $\text{Na}^+\text{CpMo}(\text{CO})_3^-$ in THF. The reaction mixture was stirred at room temperature and monitored by infrared.

5. Kinetic Measurements: RX Addition. Solutions (5 mL) of 0.029 M $\text{M}^+\text{CpMo}(\text{CO})_3^-$ were prepared in the drybox. These were syringed into a septum-capped test tube. Outside the box and temperature equilibrated, the organic halide was added via syringe (in a 20-fold excess so as to ensure pseudo-first-order reaction conditions) and timing began. In the case where the reactivity of the solvent-separated salt, $\text{Na}^+(\text{HMPA})_z^+\text{CpMo}(\text{CO})_3^-$, was to be examined, HMPA in a 20-fold excess to Na^+ was added via syringe prior to addition of RX. Similarly runs to check the effects of radical scavenging agents or added salts were prepared by adding a 20-fold excess of such reagents to the carbonylate prior to addition of RX. Samples (0.2 mL) were periodically withdrawn and the rates monitored by the observed decrease in intensity of the infrared absorbance at 1896 cm^{-1} . A minimum of ten data points was obtained for each kinetic run. Rate constants were calculated using a linear least-squares program for the pseudo-first-order rate plots of $\ln(A_t - A_\infty)$ vs. time, where A_t is the absorbance at time t and A_∞ is the absorbance at time infinity. The observed rate constants, the standard deviation, and the error at the chosen confidence limit were calculated using standard computer programs. Second-order rate constants were obtained by dividing k_{obsd} by $[\text{RX}]$. Products were identified by their infrared spectra as compared to spectra of known compounds.

6. Magnetic Resonance Sample Preparation. a. ^{13}C NMR Sample Preparation. Samples of 0.12 M $\text{M}^+\text{CpMo}(\text{CO})_3^-$ heavily enriched in ^{13}CO in THF, where $\text{M} = \text{Na}, \text{Li}$, and PPN, were evacuated and sealed in 10-mm NMR tubes. Spectra were taken both at room temperature and at -70°C .

b. ^{17}O NMR Sample Preparation. Samples of 1.4 M $\text{M}^+\text{CpMo}(\text{CO})_3^-$ were prepared in sealed 12-mm NMR tubes. At this concentration the lithium and sodium salt approached their solubility limit in the solvents used: THF, DME, and CH_3CN . The samples were sent to Mr. Robin Kump and Professor L. J. Todd of Indiana University for natural abundance ^{17}O NMR analysis. The spectra were taken within a week of preparation even though the solutions were stable for weeks.

c. ESR Samples. Samples for electron spin resonance spectra were prepared using the same concentration as for the kinetic runs.

d. Calculations. All machine calculations were carried out at the Tulane University Computing Center on a DEC 20 computer. Force constant calculations were based on the assumptions of Cotton and

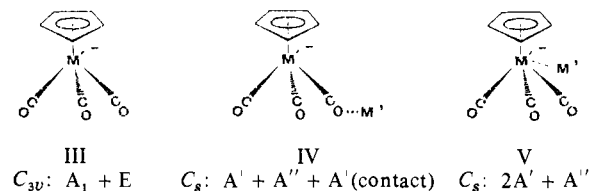
Kraihanzel¹⁷ and, in the case of ^{13}CO -enriched molecules, trial force constants were refined by iteration of a set of force constants common to a group of isotopically substituted molecules to simultaneously give a least-squares fit (to within 1 cm^{-1}) between the observed and calculated frequencies for all the molecules.^{18,19}

Results and Discussion

Infrared Spectral Measurements: Structures of the Ion Pairs.

The prevalent feature of the $\nu(\text{CO})$ IR spectra of the alkali salts of all $\text{CpM}'(\text{CO})_3^-$ anions in pure THF solutions (dielectric constant, $D = 7.4$ (25°C)) was a low-frequency band indicative of $\text{M}'\text{-C}\equiv\text{O}\cdots\text{M}^+$ interaction. This band position is cation dependent (Table I) with the Li^+ cation giving $\nu(\text{CO})$ of $\text{M}'\text{-C}\equiv\text{O}\cdots\text{Li}^+$ at ca. 1715 cm^{-1} , whereas the analogous absorption of CO interacting with Na^+ or K^+ is at 1742 or 1748 cm^{-1} , respectively. In THF solutions to which 20 equiv of HMPA as added, the three (Na^+ and K^+ salts) or five (Li^+ salts) band spectra (Table I) are simplified to spectra consisting of only two absorptions. These band positions are characteristic of the carbonylate existing in a symmetrical solvent environment, i.e., the C_{3v} structure III. The

$\nu(\text{CO})$ IR Expectations



higher frequency A_1 band is to slightly lower frequencies than is the A' band of the contact ion pair, IV; and the E vibration is intermediate between the A'' and A' ($\text{CO}\cdots\text{M}^+$) of the C_s structure, IV. As Figure 1 shows, the intensity of the E vibration corresponds to the collapse of the A'' and A' ($\text{CO}\cdots\text{M}^+$) absorptions into that one vibration. The infrared data thus suggest structure IV to dominate for Li^+ , Na^+ , and K^+ salts of all $\text{CpM}'(\text{CO})_3^-$ in THF solution. There is no indication of cation penetration of the coordination sphere yielding a ion-paired structure V, analogous to the known structure of $\text{Zn}[\text{CpMo}(\text{CO})_3]_2$,²⁰ or to one of the ion-paired forms of $\text{CpFe}(\text{CO})_2\text{-Na}^+$.^{7,8}

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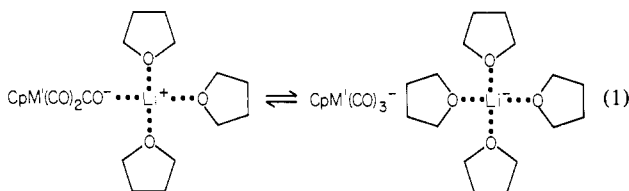
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Table I. $\nu(\text{CO})$ Infrared Data^a for $\text{M}^+\text{CpM}'(\text{CO})_3^-$ in THF Solution

salt	A'	A ₁	A''	E	A'(CO...M ⁺)
Li ⁺ CpMo(CO) ₃ ⁻	1907	1900 sh ^b	1808	1783 m ^b	1717
Na ⁺ CpMo(CO) ₃ ⁻	1899		1796		1743
K ⁺ CpMo(CO) ₃ ⁻	1897		1798		1748
M ⁺ ·HMPA _x CpMo(CO) ₃ ⁻		1898 ^c		1781 ^c	
PPN ⁺ CpMo(CO) ₃ ⁻		1896		1780	
Li ⁺ CpCr(CO) ₃ ⁻	1903	1894 sh ^b	1805	1779 m ^b	1715
Na ⁺ CpCr(CO) ₃ ⁻	1897		1793		1743
K ⁺ CpCr(CO) ₃ ⁻	1895		1788		1745
M ⁺ ·HMPA _x CpCr(CO) ₃ ⁻		1895 ^c		1778 ^c	
Li ⁺ CpW(CO) ₃ ⁻	1903	1902 ^b	1803	1786 ^b	1716
Na ⁺ CpW(CO) ₃ ⁻	1896		1792		1742
K ⁺ CpW(CO) ₃ ⁻	1894		1784		1748
M ⁺ ·HMPA _x CpW(CO) ₃ ⁻		1894 ^c		1779 ^c	

^a Symmetry labels A', A'', and A'(CO...M⁺) belong to contact ion pairs in which the carbonylate is of C_s symmetry. The A₁ and E labels are for the symmetrically solvated or nonperturbed carbonylates of symmetry C_{3v}. Intensity ratios of A':A'':A'(CO...M⁺) are roughly 1:1:1. Intensity ratios of A₁:E are ca. 1:2. Frequency values are good to ± 2 cm⁻¹. ^b Lithium salts exist as a mixture of contact and solvent-separated ion pairs in THF. The latter are estimated to be 20–25% of the former for each CpM'(CO)₃⁻. ^c Solutions of all M⁺CpM'(CO)₃⁻ (M⁺ = Li⁺, Na⁺, K⁺) to which a 20-fold excess of HMPA was added exhibited the same $\nu(\text{CO})$ maxima to within ± 1 cm⁻¹.

Indeed the cation of greatest Z⁺/r₊ ratio, Li⁺, displays the greatest propensity for solvent-separated ion-pair formation. The five-band $\nu(\text{CO})$ IR spectra observed for Li⁺ salts of all CpM'(CO)₃⁻ in THF are due to a mixture of structures III and IV in ratio of ca. 1:4. Not inconsistently, the Li cation perturbs the anions most, as demonstrated by the low $\nu(\text{CO})$ of the M'—CO...Li⁺ vibration, and also interacts best with the THF solvent molecules, hence yielding the spectrally observable equilibrium represented by eq 1.

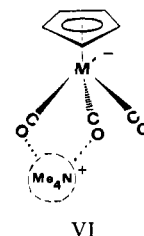


With the more polar solvent CH₃CN (*D* = 35.99, 25 °C), the M⁺CpM'(CO)₃⁻ salts display $\nu(\text{CO})$ IR indicative of a symmetrical solvent field about CpM'(CO)₃⁻. The $\nu(\text{CO})$ band positions are practically identical with those of structure III in THF, achieved by the addition of HMPA to alkali salts.

The $\nu(\text{CO})$ IR spectra of PPN⁺ salts of CpMo(CO)₃⁻ in THF also show the two-band spectrum typical of the unperturbed anion, structure III. The tetramethylammonium salt, however, shows a more complex $\nu(\text{CO})$ infrared spectrum in THF. The high-frequency absorption at 1895 cm⁻¹ has a definite shoulder at ca. 1906 cm⁻¹ and there is a continuous broad absorption between 1800 and 1700 in which one might discern three maxima: 1795 (sh), 1779, and 1760 cm⁻¹. On addition of HMPA, a sharp two-line spectrum emerges with absorptions at 1897 and 1779 cm⁻¹ indicative of structure III. The interpretation is that in THF some contact of the anion by Me₄N⁺ perturbs the CpMo(CO)₃⁻ symmetry. The broad bands were not amenable to unambiguous band resolution.

An X-ray crystal structure analysis of Me₄N⁺CpCr(CO)₃⁻ has been reported.²¹ Although the CO ligands of the anion are of identical bond lengths, one hydrogen of the Me₄N⁺ cation is within the van der Waals contact distance of a carbonyl oxygen. It is possible that in solvents of low polarity closer ion-pair contact exists than in the solid state where multiple anion/cation forces and packing forces enforce a rigidity of structure not required in the solution phase. Whether in THF solution the Me₄N⁺ cation interacts with a single carbonyl oxygen, as do alkali cations (structure IV), or with two CO oxygens, as do cations of modified electrostatic potential² (structure VI), was not determined. It is clear that at least two types of CpMo(CO)₃⁻ ion sites exist in THF

solution when Me₄N⁺ is the counterion, one of structure III and the second most probably of type IV or VI.



Conductivity Measurements: Nature of the Symmetrically Solvated or Non-Cation-Perturbed Carbonylate III. It has been noted many times that the infrared technique of determining solution environment around a transition metal carbonylate is sensitive only to the presence of an interacting cation in the first solvent-shell environment. Complexation of a small potentially interacting cation such as Na⁺ or Li⁺ by a molecule such as HMPA essentially places the carbonylate in a hydrocarbon environment. The IR technique cannot distinguish between one solvent molecule separating cation from anion (i.e., a solvent-separated ion pair as is the product of eq 1) and thousands of solvent molecules separating cation from anions (free ions). The equivalent conductance of THF solutions of various salts of CpMo(CO)₃⁻ shows a dependence on concentration very similar to those reported earlier.³ Using the Fuoss equations and data collected in precisely the same manner as described previously,^{3,22} ion-pair dissociation constants were determined for PPN⁺-CpMo(CO)₃⁻, Me₄N⁺ CpMo(CO)₃⁻, and Na⁺CpMo(CO)₃⁻ to be 7.8 × 10⁻⁵, 2.9 × 10⁻⁶, and 4.1 × 10⁻⁶ M, respectively. It is not certain that the difference in K_D values is greater than the experimental error of these measurements, estimated at $\pm 10\%$. Assuming, however, that the difference is real, the greater association of Me₄N⁺ vs. Na⁺ for CpMo(CO)₃⁻ is most likely due to the fact that the Na⁺ ion is highly solvated in the concentration range studied conductometrically (10⁻⁴–10⁻⁶ M). The Na⁺-CpMo(CO)₃⁻ is expected to exist largely as solvent-separated ion pairs at these concentrations. The Me₄N⁺ ion, on the other hand, is much less likely to interact well with THF than is Na⁺. Hence it is quite possible that more extensive association with anion exists for Me₄N⁺ than with [Na⁺·THF]_x.

The large PPN⁺ shows an ion-pair dissociation constant of 7.8 × 10⁻⁵ M, which is a larger number than that of the Me₄N⁺ or Na⁺ salts to be sure, but undoubtedly extensive ion pairing exists in the PPN⁺ salts. In analogy with our earlier conductivity studies of THF and THF/HMPA solutions of NaMn(CO)₅, it is expected that Na(HMPA)_x⁺CpMo(CO)₃⁻ exists as solvent-separated ion pairs in THF. Thus the two large counterions PPN⁺ and

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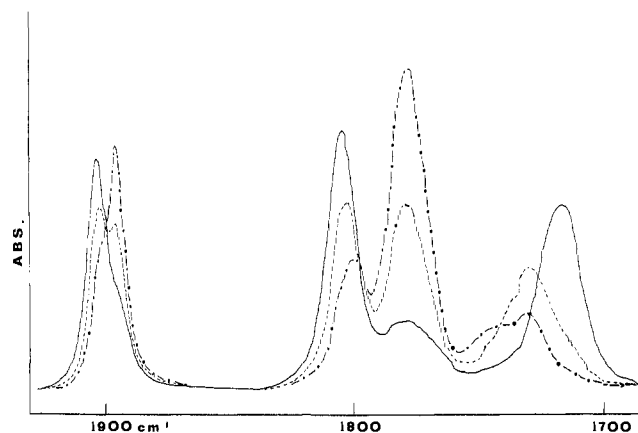
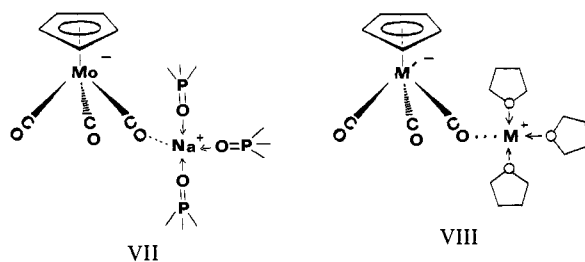


Figure 2. $\nu(\text{CO})$ IR spectra of $\text{Li}^+\text{CpCr}(\text{CO})_3^-$ in THF (0.03 M) as a function of incremental addition of HMPA. —, pure THF; ---, plus 1 equiv of HMPA; —·—, plus 2 equiv of HMPA.

$\text{Na}^+(\text{HMPA})_x$ are associated with, but not perturbing of, the carbonylate.

Infrared Spectral Measurements: Specific Solvation of the Alkali Cations. Lithium salts of $\text{CpM}'(\text{CO})_3^-$ were slightly soluble in Et_2O ($D = 4.2$ at 25°C) solution. The complex $\nu(\text{CO})$ IR spectra obtained on dilute solutions were indicative of strong contact-ion-pair interactions of the type illustrated by IV or VI and possibly triple ion formation. Addition of incremental amounts of HMPA completely solubilized the $\text{Li}^+\text{CpM}'(\text{CO})_3^-$ as well as the Na^+ and K^+ salts, initially drawing them into solution, with ca. 10 equiv of HMPA, as cation solvated contact ion pairs, VII. (The ion



pair illustrated by VII is drawn for convenience. An evaluation of the specific coordination number of Na^+ as solvates of directed oxygen donor ligands is solvent dependent and on the order of 4 to 6.²³ Larger amounts of HMPA promoted the carbonylate in the C_{3v} structure III form, i.e., solvent-separated ion pairs. The ease with which the separation of ion pairs occurs, i.e., the amount of HMPA required, is by and large independent of M' but dependent on M^+ with Li^+ , requiring less HMPA to attain total solvent separated status and $\text{Li}^+ < \text{Na}^+ \approx \text{K}^+$ (the latter requiring >25 equiv of HMPA).

The $\nu(\text{CO})$ IR spectra of the cation-solvated contact ion pairs in Et_2O indicated that HMPA significantly modified the electrostatic potential of the cation as compared to its potential in the form illustrated by VIII. For example, structure VII with $\text{M}' = \text{W}$ and $\text{M}^+ = \text{Na}^+$ and K^+ has A' ($\nu(\text{CO}\cdots\text{M}^+)$) bands at 1750 and 1756 cm^{-1} respectively, some 8 cm^{-1} higher than the analogous VIII structural types. It is reasonable to assume that the mass effect on $\nu(\text{CO})$ is similar for $\text{M}^+(\text{O}=\text{P}(\text{NMe}_2)_3)_n$ and $\text{M}^+(\text{THF})_n$ and that the increase in $\nu(\text{CO})$ reflects the difference in the ability of the cation at its available open site to interact with the carbonyl oxygen.²⁴⁻²⁶

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(24) The $\nu(\text{CO})$ of $\text{Mo}-\text{CO}\cdots\text{Na}^+\text{py}_x$ ($\text{py} = \text{pyridine}$) is reported²⁵ to be 1749 cm^{-1} . Highly organized solvated ion pairs are known for $\text{py}_4\text{Mg}[\text{CpMo}(\text{CO})_3]_2^{25}$ and for $(\text{THF})_4\text{Mg}[\text{CpMo}(\text{CO})_3]_2$.²⁶ For the former, X-ray crystal structure analysis shows that octahedral coordination of the Mg^{2+} is achieved by a planar arrangement of N donor atoms and the fifth and sixth coordination sites are assumed by carbonylate oxygens. The $\nu(\text{CO})$ of $\text{Mo}-\text{CO}\cdots\text{Mg}^{2+}(\text{THF})_4\cdots\text{OC}-\text{Mo}$ and the tetrapyrroline analogue are at 1680 and 1665 cm^{-1} , respectively.

Table II. Cotton-Kraihanzel Force Constants for Carbon Monoxide Stretching Vibrations of $\text{CpMo}(\text{CO})_3^-$ Salts in THF Solutions^a

salt	k	k'	k_1	k_1'
$\text{PPN}^+\text{CpMo}(\text{CO})_3^-$	13.35_s		0.57_b	
$\text{CpMo}(\text{CO})_2\text{CO}\cdots\text{Na}^+$	13.64_7	12.53_6	0.62_3	0.54_1
$\text{CpMo}(\text{CO})_2\text{CO}\cdots\text{Li}^+$	13.82_1	12.10_3	0.63_3	0.51_4

^a k is defined as the stretching force constant for nonperturbed CO groups and k' for the alkali contacted group $\text{Mo}^--\text{CO}\cdots\text{M}^+$. k_1 is the interaction constant between CO groups which are not contacted by alkali cations and k_1' is the interaction constant between $\text{Mo}^--\text{CO}\cdots\text{M}^+$ and a nonperturbed $\text{Mo}-\text{CO}$ group.

Not unexpectedly such positive charge neutralization by good alkali cation donor ligands such as HMPA was most dramatically demonstrated in lithium salts of the carbonylates. On addition of incremental amounts of HMPA to THF solutions of $\text{LiCpCr}(\text{CO})_3$, the high-frequency $\nu(\text{CO})$ bands of the contact ion pair, A_1 and A_1' , were observed to diminish in intensity and move to slightly lower wavenumbers while the low-frequency A_1 band representative of $\text{Cr}-\text{CO}\cdots\text{Li}^+(\text{THF})_x$ resolutely marched to higher frequencies (Figure 2) as the mixed solvates, $\text{Cr}-\text{CO}\cdots\text{Li}^+(\text{THF})_{x-1}(\text{HMPA})_1$, etc., formed. Note that with each increment of HMPA added, the bands assigned to the carbonylate in a symmetrical solvent environment, structure III, gained intensity. As discussed above, the bands at ca. 1895 and 1780 cm^{-1} are indicative of $\text{CpCr}(\text{CO})_3^-\cdot\text{THF}\cdot\text{Li}^+$ or $\text{CpCr}(\text{CO})_3^-\cdot\text{HMPA}\cdot\text{Li}^+$, and the IR technique is unable to distinguish between these possibilities.

Addition of a third equivalent of HMPA to THF solutions of $\text{LiCpCr}(\text{CO})_3$ converted $>90\%$ of all contact ion pairs to solvent-separated forms. For Na^+ and K^+ salts, 10 and 12 equiv of HMPA, respectively, were required to promote the same amount of solvent separation. Hence the equilibrium constants involving complexation of the cations by HMPA diminish as do the cations' Z^+/r_+ ratios, $\text{Li}^+ > \text{Na}^+ \geq \text{K}^+$.

Although the dielectric constant of CH_3CN ($D = 36$) is almost equal to that of HMPA ($D = 38$), the former does not show the highly specific alkali cation complexing ability of the latter. The experiment analogous to that shown in Figure 1 required addition of 400 equiv of CH_3CN (which is ca. 30% by volume of the total $\text{CH}_3\text{CN}/\text{THF}$ solution) in order to solvent separate $\text{NaCpMo}(\text{CO})_3$.

Infrared Spectral Measurements: Force Constant Calculations. Carbonyl stretching force constants of $\text{CpMo}(\text{CO})_3^-$ salts in THF were calculated by the Cotton-Kraihanzel method¹⁷ and refined by fitting calculated to observed bands for ^{13}C -enriched carbonylates.^{18,19} Examples of the fit are given in Table II and the restricted force field CO stretching force constants are given in Table III. The lower value for $\text{CpMo}(\text{CO})_3^-$ as compared to those of other monoanionic carbonylates which have been determined (e.g., $\text{Mn}(\text{CO})_5^-$,³ $\text{LMn}(\text{CO})_4^-$,³ $\text{Hf}(\text{CO})_4^-$,⁵ and $\text{LV}(\text{CO})_5^-$ ⁶) roughly reflects the distribution of negative charge onto a smaller number of carbonyl ligands. The greater perturbation of $\text{CpMo}(\text{CO})_3^-$ by Li^+ vs. Na^+ is evident from the differences between the force constant of the nonperturbed $\text{CpMo}(\text{CO})_3^-$ and that of the cation-contacted CO group in $\text{CpMo}(\text{CO})_2\text{CO}\cdots\text{M}^+$. With $\text{M}^+ = \text{Li}^+$ the difference is $1.25\text{ mdyn}/\text{\AA}$; with $\text{M}^+ = \text{Na}^+$, $0.82\text{ mdyn}/\text{\AA}$.

Magnetic Resonance Studies: Carbon-13 and Oxygen-17 NMR. The carbon-13 nuclear magnetic resonance spectra of $\text{CpMo}(\text{CO})_3^-$ salts in THF solution were independent of cation (Li^+ , Na^+ , and PPN^+) and of temperature ($+23^\circ$ and -70 to -80°C). In all cases sharp resonances were observed at $236.2 \pm 0.4\text{ ppm}$ downfield from Me_4Si , assignable to the carbonyl carbons; and at 86.4 ppm , assignable to the Cp ring carbons. The carbonyl resonances are ca. 6 ppm downfield from the average of CO resonances of $[\text{CpMo}(\text{CO})_3]_2$ adding to the data revealing that

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Table III. Calculated and Observed $\nu(\text{CO})$ Frequency Data for $\text{PPN}^+\text{CpMo}(\text{CO})_3^-$ and $\text{Na}^+\text{CpMo}(\text{CO})_3^-$ in THF ($\circ = {}^{12}\text{CO}$; $\bullet = {}^{13}\text{CO}$)

species	calculated	observed
	1896	1896
	1779	1780
	1884	1884
	1750	1751
	1779	1780
	1871	1869
	1782	1763
	1739	1739
	1853	1852
	1739	1739

	1899	1901
	1796	1797
	1742	1743
	1884	1884
	1774	1774
	1737	1738
	1895	1897
	1796	1795
	1707	1708
	1863	1864
	1756	1756
	1735	1738
	1879	1879
	1773	1770
	1704	1703
	1857	1856
	1756	1755
	1703	1701

signals of the anionic carbonyls are found downfield from analogous neutral carbonyls. The shift of the CO resonances of $\text{CpMo}(\text{CO})_3^-$ to ca. 11 ppm upfield from its $\text{CpCr}(\text{CO})_3^-$ congener reflects the metal triad effect that has been previously reported in ${}^{13}\text{C}$ NMR studies.²⁷ The carbonyl carbon resonances of $\text{CpCr}(\text{CO})_3^-$ are similarly shifted downfield from isoelectronic neutral analogues $\text{CpMn}(\text{CO})_3$ and $\text{MeCpMn}(\text{CO})_3$.²⁸

Oxygen-17 resonances of Li^+ and Na^+ salts of $\text{CpMo}(\text{CO})_3^-$ also had very similar chemical shifts in THF solution, each showing only one resonance at 352.4 ± 0.1 and 351.8 ± 0.1 ppm downfield from the H_2O standard, respectively. In DME and CH_3CN in which the $\text{Na}^+\text{CpMo}(\text{CO})_3^-$ salt displayed IR spectra identical with $\text{PPN}^+\text{CpMo}(\text{CO})_3^-$ in THF, the O-17 resonances were shifted slightly more downfield to 356.0 and 356.6 ppm, respectively. The oxygen signals for the anions show a large, ca. 50 ppm, upfield shift from the average of the CO resonances for $[\text{CpMo}(\text{CO})_3]_2$.²⁹ In general, O-17 NMR chemical shifts are opposite to the C-13 shifts for a series of compounds.³⁰ That is,

(27) Bodner, G. M.; Todd, L. J. *Inorg. Chem.* **1974**, *13*, 1335.

(28) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* **1974**, *77*, 1.

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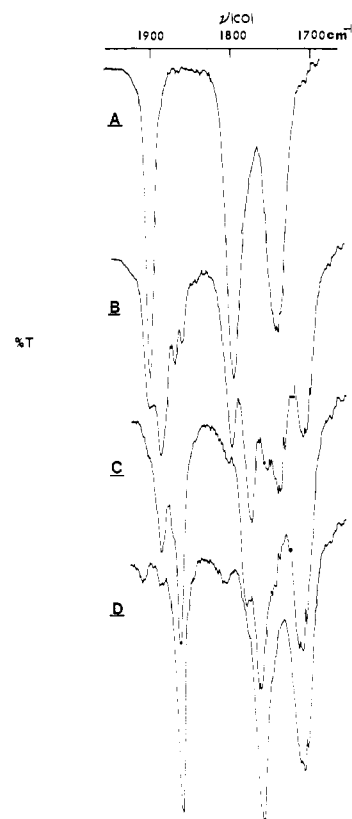
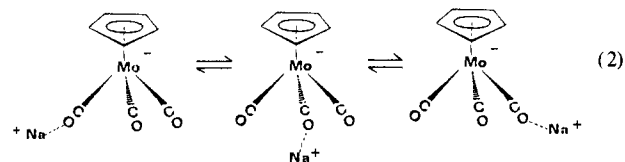


Figure 3. ${}^{13}\text{CO}$ exchange reaction with $\text{Na}^+\text{CpMo}(\text{CO})_3^-$ in THF: A, $\text{Na}^+\text{CpMo}({}^{12}\text{CO})_3^-$; B, reaction time = 12 min; C, reaction time = 36 min; D, reaction time = 180 min or final spectrum.

as in proton resonances, oxygen-17 chemical shifts usually indicate increased shielding (chemical shifts to higher fields) as more negative charge is placed onto the atom containing the NMR-active nucleus. Sufficient O-17 NMR data of anions are not available to warrant a detailed discussion of the solvent effects or cation effects observed here. It is nevertheless interesting to note that the direction of O-17 chemical shift differences in the Na^+ or Li^+ contact vs. structure III form of $\text{CpMo}(\text{CO})_3^-$ is consistent with CO force constant changes. The weighted averages $((2k_{\text{CO}} + k_{\text{CO}'})/3)$ of contact ion paired forms are smaller than k_{CO} of the symmetrical C_{3v} form (Table III). The $\text{CpMo}(\text{CO})_3^-$ responds to the interacting alkali cations not only by rearranging the available electron density in the $\text{Mo}(\text{CO})_3^-$ unit, but also by allowing more electron density from Mo or CpMo to drain onto the carbonyl ligands.

The outstanding NMR result is the fact of a single carbonyl resonance in both the O-17 and C-13 spectra, indicating a lifetime of any one $\text{CpMo}(\text{CO})_2\text{CO}\cdots\text{M}^+$ interaction (eq 2) shorter than



the time scale of the NMR experiment, ca. 10^{-2} s.³¹ The lower limit of the lifetime of a particular ion site may be taken as the mean lifetime of a collision pair which is on the order of 10^{-11} s,³² obviously detectable by IR. Carbon-13 was successful as an indicator of contact ion pairing at an acyl or formyl oxygen site of $\text{M}^+\text{Fe}(\text{CO})_4(-\text{C}(\text{O})\text{R})^-$.³³ Chemical shift differences with M

(31) The time scale of the ${}^{17}\text{O}$ NMR experiment has been shown to be approximately the same as that of the ${}^{13}\text{C}$ NMR experiment: Kump, R. L.; Todd, L. J., submitted for publication.

(32) Benson, S. W. "The Foundations of Chemical Kinetics"; McGraw-Hill: New York, 1960; pp 495, 496.

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Table IV. Counterion Dependence of the Reaction of ^{13}CO with $\text{M}^+\text{CpMo}(\text{CO})_3^-$ in THF at $22 \pm 1^\circ\text{C}$

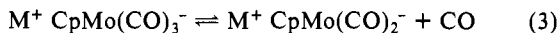
entry	M^+	partial pressure (^{13}CO), ^a atm	$t_{1/2}$ (min) ^b	k_1 (s^{-1}) ^c
1	Li^+	1	17.5 ± 2.5	6.6×10^{-4}
2	Na^+	1	40 ± 5	2.9×10^{-4}
3	Na^+	0.6^d	40 ± 5	2.9×10^{-4}
4	Na^+	0.5^d	40 ± 5	2.9×10^{-4}
5	PPN^+	1	100 ± 10	1.05×10^{-4}

^a Except where noted, the reactions were run in an atmosphere of 93.7% ^{13}CO . ^b Half-lives are based on the appearance of $\text{CpMo}(\text{CO})_3^-$. The time required to achieve 75% enrichment was taken as $2t_{1/2}$. ^c First-order rate constants are based on the $t_{1/2}$ measurements and thus have errors of the same order of magnitude. ^d Ar was added to these flasks to bring the total pressure to 1 atm.

= Na^+ vs. PPN^+ in this case do not signify a static sodium-oxy-carbene ligand structure for the sodium form but rather a dynamic and highly specific interaction of the Na^+ cation with the very basic formyl or acyl oxygen. The equivalence of all three CO groups of $\text{CpMo}(\text{CO})_3^-$ dictates equal site populations as shown in eq 2.

Chemical Reactivity: Ligand-Exchange Studies. During the preparation of samples enriched in carbon-13 for NMR analysis, it was noted that the rate of this ligand-exchange process was counterion dependent. An abbreviated infrared monitor of the ^{13}CO incorporation into $\text{Na}^+\text{CpMo}(\text{CO})_3^-$ in THF solution is given in Figure 3. The initial three-band spectrum for $\text{CpMo}(\text{CO})_3^-$ (^{12}CO)₂(^{13}CO ... Na^+) is very similar to the designated final three-band spectrum of $\text{CpMo}(\text{CO})_3^-$ (^{13}CO)₂(^{12}CO ... Na^+). The reversibility of the exchange and purity of the product were demonstrated by adding ^{12}CO to the C-13 enriched product which afforded the spectrum, identical in intensity, of the original all ^{12}CO carbonylate. Intermediate complex spectra are shown in Figure 3 which indicate bands for the species $\text{CpMo}(\text{CO})_3^-$ (^{13}CO)₂(^{12}CO)₂⁻ and $\text{CpMo}(\text{CO})_3^-$ (^{13}CO)₂(^{12}CO)⁻ in their various contact ion-paired forms. Band assignments may be found in Table II. The force-constant analysis described earlier (Table III) utilized these spectra.

Table IV presents relatively crude rate data for the incorporation of ^{13}CO into various salts of $\text{CpMo}(\text{CO})_3^-$. The reactions were monitored to ca. 75% enrichment; i.e., the band area of the $\text{CpMo}(\text{CO})_3^-$ species was 75% that of the $\text{CpMo}(\text{CO})_3^-$ at $t = 0$, and the time required was taken as two half-lives. Entries 2–5 of Table IV suggest that the exchange process follows a dissociative mechanism, eq 3, where rate decrease is in the order $\text{M}^+ = \text{Li}^+ > \text{Na}^+ > \text{PPN}^+$.



The counterion dependence is supportive of the dissociative mechanism of (3). The electronic migration experienced by the carbonylate in going from structural type III to IV should serve to enhance the Mo–C bond of Mo–CO... M^+ but to diminish the Mo–C bond of those Mo–CO groups not interacting with a cation, stabilizing the latter.

Attempts to capture the coordinatively unsaturated $[\text{CpMo}(\text{CO})_2^-]$ with phosphorus ligands, PPh_3 and $\text{P}(\text{O}^i\text{Pr})_3$, were unsuccessful. Thus a 20-fold excess of the P ligand to $\text{CpMo}(\text{CO})_2\text{CO}^-$... Na^+ in THF yielded no products in a time period sufficient to see complete ^{13}CO exchange. The conditions of the latter reaction were the same except the CO concentration was on the order of 0.01 M,^{34,35} or one-half the concentration of $\text{CpMo}(\text{CO})_3^-$. Since the atmosphere above the stirred solution was ^{13}CO , it was assumed that the level of dissolved CO remained

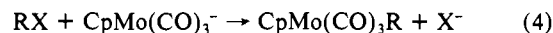
(34) The concentration of CO in CO-saturated THF was estimated by the procedure of Osburn and Markovic³⁵ to be 8.8×10^{-3} M, using data appropriate at 20°C . The temperature at which the CO exchange reactions were run was $22 \pm 1^\circ\text{C}$.

(35) Osburn, J. O.; Markovic, P. L. *Chem. Eng. (N.Y.)* **1969**, 76 (18), 105.

essentially constant, but nevertheless small when compared to $[\text{PPh}_3]$ or $[\text{P}(\text{O}^i\text{Pr})_3]$ in the P-ligand “exchange” reactions. With long reaction periods, 7–28 h, and with Ar-purging to remove dissolved CO, new carbonyl-containing products appeared in the P ligand/ $\text{CpMo}(\text{CO})_3^-$ solutions. A spectral match with known possible products such as $\text{CpMo}(\text{CO})_2\text{P}^-$ or $\text{Cp}_2\text{Mo}_2(\text{CO})_4\text{P}_2$ was not illuminating.^{7,36}

It therefore appears that the coordinatively unsaturated anion $[\text{CpMo}(\text{CO})_2^-]$ is much more discriminating toward incoming ligands, preferring the good π -accepting CO over poorer π -accepting and/or better σ -donating P ligands, than are neutral 16-electron analogues.^{37–39} A study of this phenomenon is underway.⁴⁰

Chemical Reactivity: Oxidative Addition of RX to $\text{CpMo}(\text{CO})_3^-$. Reactions of benzyl chloride, benzyl bromide, *n*-BuI, and *n*-BuBr with salts of $\text{CpMo}(\text{CO})_3^-$ (eq 4) were carried out under pseu-



$$\text{rate} = k_2[\text{M}^+\text{CO}^-][\text{RX}] \quad (5)$$

do-first-order conditions for the metal carbonylate with $[\text{RX}]$ generally at a 40-fold excess, and monitored with time. Plots of $\ln(A_t - A_\infty)$ of the ca. 1900-cm^{-1} $\nu(\text{CO})$ band of $\text{CpMo}(\text{CO})_3^-$ vs. time were linear over the entire reaction. A first-order dependence on $[\text{RX}]$ was established by varying $[\text{RX}]$ from a 15- to a 40-fold excess in which cases a constant value for $k_2 = k_{\text{obsd}}/[\text{RX}]$ was obtained. Second-order rate constants for the reactions studied are found in Table V.⁴¹

The results of Table V may be summarized as follows. In agreement with our earlier study, as well as the work of Cassar et al.,¹² the reaction of $\text{CpMo}(\text{CO})_3^-$ with BzI proceeded most rapidly when the carbonylate was polarized by Na^+ as opposed to being in a symmetrical solvent environment as it is when the counterion is $\text{Na}^+(\text{HMPA})_x$. The reaction of *n*-butyl halides with $\text{CpMo}(\text{CO})_3^-$ showed the opposite counterion effect (entries 1–7, Table V). The THF solution of $\text{Na}^+\text{CpMo}(\text{CO})_3^-$ containing a 20:1 molar ratio of $\text{HMPA}:\text{Na}^+$ showed an enhancement of the rate of reaction (eq 4) some 15 times over that of pure $\text{Na}^+\text{CpMo}(\text{CO})_3^-$. A smaller cation effect was noted for the similar and slower reactions with *n*-BuBr, with $k_2(\text{Na}^+(\text{HMPA})_x):k_2(\text{Na}^+) \approx 5:1$ (entries 6 and 7). The reaction of *n*-BuCl with $\text{CpMo}(\text{CO})_3^-$ was too slow to follow accurately, and with the better nucleophile, $\text{Na}^+\text{CpFe}(\text{CO})_2^-$, reactions were very fast. Qualitatively, however, we found the rate of reaction of *n*-BuCl with $\text{Na}^+\text{CpFe}(\text{CO})_2^-$ in pure THF to be about one-fifth as great as the analogous reaction of solvent-separated $\text{Na}^+(\text{HMPA})_x^+\text{CpFe}(\text{CO})_2^-$.⁴²

The data of Figure 4 demonstrated that the HMPA served to specifically bind the Na^+ and thus changed the reactivity and structure of $\text{CpMo}(\text{CO})_3^-$ owing to a change in local solvent or cation environment rather than to a bulk solvent dielectric constant change. The variation of k_2^{obsd} value (see Figure 4 caption for definition of k_2^{obsd}) with incremental additions of HMPA showed a significant increase as the $\text{HMPA}:\text{Na}^+$ ratio went to 20:1 (corresponding to ca. 2.4% (v/v) of HMPA in the THF).

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(40) Hanckel, M.; Schumann, B.; Darenbourg, M. Y., unpublished results.

(41) Entries 1, 2, 6, and 7 of Table V are repeats of kinetic runs reported in a preliminary communication of this work.¹³ Minor discrepancies in values are due to a change in monitoring instrumentation. The published values were taken from data obtained on a Perkin-Elmer 521 spectrophotometer whose IR beam generated a considerably higher temperature (ca. 37°C) at the sample during the required scanning time than does the Perkin-Elmer 283-B (ca. 25°C) which is now used.

(42) In pure THF the $\text{Na}^+\text{CpFe}(\text{CO})_2^-$ exists as a mixture of pairs of the form $\text{CpFe}(\text{CO})(\text{CO})^-$... Na^+ and of even more closely interacting forms apparently having some Fe^- ... Na^+ interaction.^{7,8}

Table V. Second-Order Rate Constants for Reaction of $\text{CpMo}(\text{CO})_3^-$ with Organic Halides at $22 \pm 1^\circ\text{C}$ in Tetrahydrofuran

entry	counterion	additives ^a (equiv)	RX ^b	k_2 ($\text{m}^{-1} \text{s}^{-1}$) ^c
1	Na^+		<i>n</i> -BuI	$1.33 (\pm 0.08) \times 10^{-4}$
2	$\text{Na}^+(\text{HMPA})_x$	HMPA (20)	<i>n</i> -BuI	$2.09 (\pm 0.12) \times 10^{-3}$
3	Na^+	1,4-cyclohexadiene (20)	<i>n</i> -BuI	$1.50 (\pm 0.12) \times 10^{-4}$
4	$\text{Na}^+(\text{HMPA})_x$	HMPA (20)		
5	Na^+	1,4-cyclohexadiene (20)	<i>n</i> -BuI	$1.90 (\pm 0.05) \times 10^{-3}$
6	Na^+	NaBPh_4 (10)	<i>n</i> -BuI	$1.07 (\pm 0.10) \times 10^{-4}$
7	$\text{Na}^+(\text{HMPA})_x$	HMPA (20)	<i>n</i> -BuBr ^d	$2.62 (\pm 0.14) \times 10^{-6}$
8	Na^+		<i>n</i> -BuBr ^d	$1.36 (\pm 0.03) \times 10^{-5}$
9	$\text{Na}^+(\text{HMPA})_x$	HMPA (20)	BzI	$1.29 (\pm 0.05) \times 10^{-4}$
10	Na^+	1,4-cyclohexadiene (20)	BzI	$5.01 (\pm 0.31) \times 10^{-5}$
11	$\text{Na}^+(\text{HMPA})_x$	HMPA (20)	BzI	$1.24 (\pm 0.10) \times 10^{-4}$
12	Na^+	1,4-cyclohexadiene (20)	BzI	$4.77 (\pm 0.25) \times 10^{-5}$
13	Na^+	NaBPh_4 (10)	BzI	$1.28 (\pm 0.07) \times 10^{-4}$
14	$\text{Na}^+(\text{HMPA})_x$	HMPA (20)	BzI	$3.83 (\pm 1.30) \times 10^{-3}$
			BzI	$6.28 (\pm 1.80) \times 10^{-3}$

^a Additives were added to solvent prior to initiating reaction. Numbers in parentheses are numbers of equivalents per sodium ion. ^b Reactions were run with RX in 40-fold excess of the carbonylate concentration which was 0.022 M. ^c Values of k_2 obtained from dividing the pseudo-first-order rate constant, k_{obsd} , by $[\text{RX}]$. The value reported for k_2 is the average of from two to four kinetic plots, utilizing 10–15 individual measurements per run. The error is the average of errors in individual runs. Replication was well within 10%. See text. ^d These data were taken from ref 13 and were monitored at a slightly higher temperature. See text. ^e Solutions were not removed from IR cell and temperature control was not possible. Temperature of reaction mixture within sealed cell estimated at $+30^\circ\text{C}$.

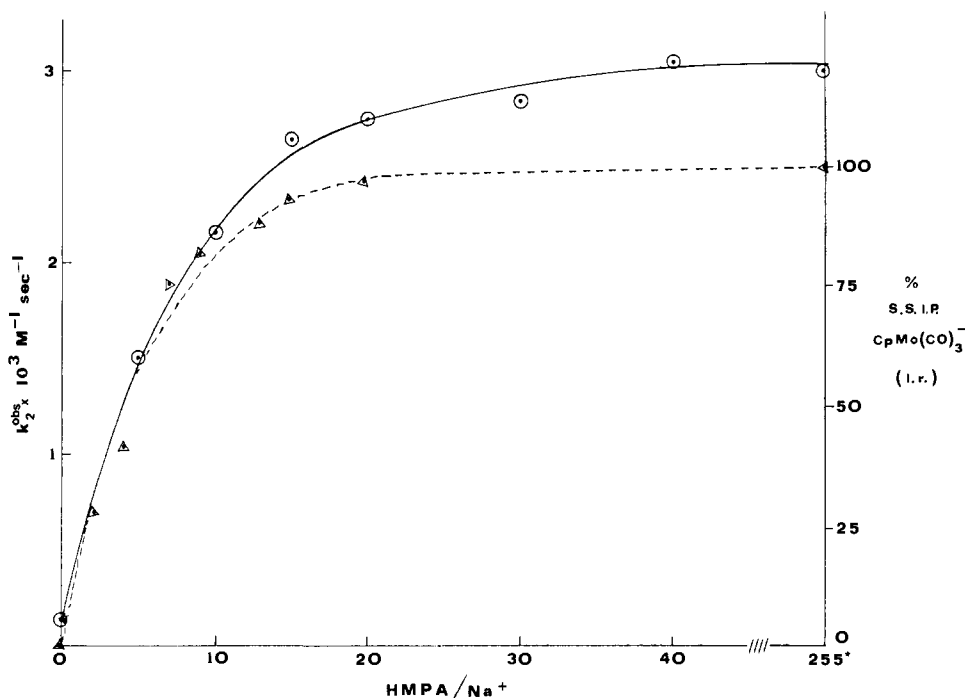


Figure 4. A plot of k_2^{obsd} values (right ordinate, —) vs. incremental additions of HMPA for the reaction of $\text{Na}^+\text{CpMo}(\text{CO})_3^-$ with *n*-BuI in THF. Superimposed is a plot of the amount of symmetrical $\text{CpMo}(\text{CO})_3^-$ (---) as determined by comparison of $\nu(\text{CO})$ band areas vs. the HMPA/ Na^+ ratio. * = pure HMPA.

Thereafter k_2^{obsd} was fairly independent of added HMPA and taken to be k_2' , the second-order rate constant for reaction of $\text{Na}(\text{HMPA})_x^+\text{CpMo}(\text{CO})_3^-$ with *n*-BuI. Simultaneously the IR monitor of the ratio of symmetrical $\text{CpMo}(\text{CO})_3^-$ vs. sodium-perturbed $\text{CpMo}(\text{CO})_2\text{CO}\cdots\text{Na}^+$ also showed an increase up to HMPA: Na^+ ratios of 20:1. The limiting value of $k_2' = 2.68 (\pm 0.10) \times 10^{-3} \text{ mol}^{-1} \text{ L}^{-1} \text{ s}^{-1}$ was experimentally the same as k_2 for reaction of *n*-BuI with $\text{PPN}^+\text{CpMo}(\text{CO})_3^-$ in pure HMPA, $2.60 (\pm 0.13) \times 10^{-3} \text{ mol}^{-1} \text{ L}^{-1} \text{ s}^{-1}$.¹³ As noted above, conductivity measurements for the latter salt have shown the large PPN^+ counterion to be highly associated with the $\text{CpMo}(\text{CO})_3^-$ in pure THF;²² however, the carbonylate is not at all electronically perturbed by its presence.

These data are interestingly compared with kinetic titration plots obtained for the reaction of $\text{Na}^+\text{Mn}(\text{CO})_5^-$ with BzI.³ In that earlier study a measure of the number of solvent-separated ion pairs was provided by a conductometric titration plot. The plot of k_2^{obsd} vs. HMPA: Na^+ ratio was the *mirror image* of the

equivalent conductance, Λ , vs. HMPA: Na^+ plot. The former showed a negative slope; the latter, indicating an increase in the equilibrium ion-pair dissociation constant as $\text{Mn}(\text{CO})_4\text{CO}\cdots\text{Na}^+$ became $\text{Na}(\text{HMPA})_x^+\text{Mn}(\text{CO})_5^-$, showed a positive slope. The major *change* in slopes for both curves occurred at HMPA: Na^+ ratios of between 3 and 4 to 1.^{43,44}

(43) The significance of the value of the HMPA/ Na^+ ratio at the major slope change must be viewed as a reflection of the collection of equilibrium constants which would describe the competition of solvent molecules and carbonylate anion for a binding site on the Na^+ . With the anionic charge distributed among 5 CO groups and the metal, the $\text{Mn}(\text{CO})_5^-$ anion is less competitive for electrostatic binding to Na^+ than is $\text{CpMo}(\text{CO})_3^-$ in which the -1 charge is essentially shared between only three CO groups and the metal. Displacement of the carbonylate by the strong alkali ion complexing agent, HMPA, is hence favored for the $\text{Mn}(\text{CO})_5^-$ counterion. Indeed the observed requirement of 3–4 equiv of HMPA for the production of solvent separated ion pairs in THF solutions of $\text{Na}^+\text{Mn}(\text{CO})_5^-$ is surprisingly consistent with the specific complexation number of 4 for $\text{Na}(\text{HMPA})_4^+$ determined by NMR techniques in *benzene* solutions of $\text{Na}^+\text{AlEt}_4^-$.⁴⁴

Entries 13 and 14 of Table V showed very similar rate constants for the reaction of Na^+ and $\text{Na}^+(\text{HMPA})_x$ $\text{CpMo}(\text{CO})_3^-$ with $\text{BzI}Br$, with the former reacting with slightly less facility than the latter. Thus the "inverse" counterion effect appears to hold only for $\text{RX} = \text{BzI}Cl$ (and allyl chloride³). Since the benzylic (or allylic) moiety is known to stabilize both radical and carbanion ion species, attempts were made to detect or rationalize such intermediates.

Strong benzyl radical ESR signals were observed during the reaction of $\text{Na}^+\text{CpFe}(\text{CO})_2^-$ with $\text{BzI}Br$, as well as upon mixing THF solutions of tropylium and trityl tetrafluoroborate with $\text{Na}^+\text{CpMo}(\text{CO})_3^-$ in THF solution.⁴⁵ Thus attempts were made to detect ESR signals on samples of the reacting systems, $\text{Na}^+\text{CpMo}(\text{CO})_3^-/\text{BzI}Cl$ and $\text{Na}^+\text{CpMo}(\text{CO})_3^-/n\text{-BuI}$ in THF and in HMPA/THF; however, no signals were observed. Radical scavenging agents were employed in an attempt to determine whether radical pathways were contributing to the reaction rate. Galvinoxyl instantaneously oxidized $\text{CpMo}(\text{CO})_3^-$, producing the $[\text{CpMo}(\text{CO})_3]_2$ parent dimer, and hence was not useful. The presence of hydroquinone in 1:1 molar ratio to $\text{NaCpMo}(\text{CO})_3$ did not affect the rate of reaction with $\text{BzI}Cl$ in THF. As Table V, entries 3, 4, 10, and 11 show, addition of 1,4-cyclohexadiene in 20-fold excess to reactions of $\text{CpMo}(\text{CO})_3^-$ with $n\text{-BuI}$ or $\text{BzI}Cl$ yielded rates with k_2 values equal within experimental error to those of the controls.

Whereas the above negative evidence for radical intermediates cannot unambiguously rule out their presence as contributing factors in these reactions, it seems reasonable to explore alternative mechanisms which might account for the different counterion effects. The alternatives are concerted mechanisms which necessarily involve several and competing factors: (a) the enhanced nucleophilicity of the anion in the presence of less tightly interacting counterions or in solvents capable of separating cation from anion; (b) cation assistance of leaving group; (c) cation modification of carbonylate structure; (d) the influence of solvent polarity on the stabilization of transition state relative to the reactants.

The effects of leaving group assistance were minimized in studies which compared the reactivity of $\text{BzI}Cl$ and $n\text{-BuI}$ with $\text{PPN}^+\text{CpMo}(\text{CO})_3^-$ in acetonitrile and in THF. In addition, leaving group assistance from THF or CH_3CN is unlikely owing to their lack of acidic protons. Therefore, the effect of solvent polarity could be examined for the reaction of non-cation-perturbed $\text{CpMo}(\text{CO})_3^-$ with RX . For $\text{RX} = n\text{-BuI}$, $k_2'(\text{CH}_3\text{CN})$ (where k_2' defined as the second-order rate constant for the reactive species, nonperturbed $\text{CpMo}(\text{CO})_3^-$) = $1.64 (\pm 0.06) \times 10^{-4}$ and $k_2'(\text{THF}) = 2.60 (\pm 0.13) \times 10^{-3}$, or a ratio $k_2'(\text{CH}_3\text{CN})$ to $k_2'(\text{THF})$ of 1 to 16. For $\text{RX} = \text{BzI}Cl$, $k_2'(\text{CH}_3\text{CN}) = 1.60 (\pm 0.10) \times 10^{-4}$ and $k_2'(\text{THF}) = 6.27 (\pm 1.2) \times 10^{-5}$, or a ratio $k_2'(\text{CH}_3\text{CN})$ to $k_2'(\text{THF})$ of 2.6 to 1.

These data lend further support to the operating of a classical $\text{S}_{\text{N}}2$ mechanism for the oxidative addition of nonactivated RX to $\text{CpMo}(\text{CO})_3^-$. The reaction of an anionic nucleophile with a neutral substrate involves a charge dispersal in the transition state. A polar solvent should stabilize the charge-localized reactant (i.e., the anionic nucleophile) more than the charge-dispersed transition state, thus increasing the energy of activation and lowering the rate of reaction.⁴⁶ The observed rate decrease for the reaction of $n\text{-BuI}$ and $\text{PPN}^+\text{CpMo}(\text{CO})_3^-$ on changing the solvent from THF ($D = 7.4$) to CH_3CN ($D = 38$) is in agreement with this expectation.

In contrast, the increase in rate of reaction of $\text{BzI}Cl$ with $\text{CpMo}(\text{CO})_3^-$ on going from THF to CH_3CN solvent suggests that charge separation is greater in the transition state than in the reactants. The importance of $\text{BzI}Cl$ bond cleavage in the transition state is implied.

The observed increase in rate for the reaction of $n\text{-BuI}$ and

$n\text{-Bu}Br$ with $\text{CpMo}(\text{CO})_3^-$ in a symmetrical solvent field (i.e., $\text{Na}^+(\text{HMPA})_x$ or PPN^+ as nonspecific interacting counterions) as opposed to the perturbed anion (Na^+ as counterion) is also in agreement with a classical $\text{S}_{\text{N}}2$ nucleophilic displacement reaction which benefits from the greater nucleophilicity experienced by the $\text{CpMo}(\text{CO})_3^-$ as the charge-neutralizing Na^+ is removed from close interaction with the anion. Our results are consistent with those of Watson and Bergman⁴⁷ who showed that the $n\text{-Bu}_4\text{N}^+\text{CpW}(\text{CO})_3^-$ salt reacted with more facility than did the Na^+ salt in reactions with $\text{CH}_3\text{C}\equiv\text{C}(\text{CH}_2)_4\text{I}$ to yield $\text{CpW}(\text{CO})_3\text{-}(\text{CH}_2)_4\text{C}\equiv\text{CCH}_3$. They are also in agreement with the work of Collman, Brauman et al.,⁹ on the addition of $n\text{-C}_{10}\text{H}_{21}\text{Br}$ to $\text{Na}_2\text{Fe}(\text{CO})_4$ in THF and THF/donor solvent mixtures. The separation of ion aggregates to yield probable species $\text{Na}^+\text{S-}[\text{NaFe}(\text{CO})_4]^-$ enhanced the rate of reaction. Furthermore, analogous reactions in the highly polar solvent *N*-methylpyrrolidinone proceeded with a reactivity increase of ca. 20000 times that of reactions in THF, again indicating the greater nucleophilicity of the more dissociated species, $\text{Na}^+||[\text{Na}^+\text{SFe}(\text{CO})_4]^{2-}$. The extensive group of substrates studied were all deactivated alkyl halides. In these systems the importance of leaving group assistance seems to be small when compared with the effect of increasing the nucleophilicity of the carbonylate achieved on separating the contact ion pairs.

The magnitude of the inverse counterion effect of $\text{RX} = \text{BzI}Cl$ is nucleophile dependent. Reaction with the weakest nucleophile $\text{Co}(\text{CO})_4^-$ showed the largest inverse effect (a 420-fold reduction of rate upon addition of crown ether),¹² and the stronger nucleophiles $\text{Mn}(\text{CO})_5^-$ and $\text{CpMo}(\text{CO})_3^-$ showed smaller effects (\sim tenfold and threefold rate reductions, respectively, on addition of crown ether³ or HMPA). That is, strong nucleophiles less efficiently distinguish between the subtle effects of counterions.

Taken altogether, we feel the results presented here further support the contention that cation assistance is of substantial importance in oxidative addition reactions where the RX molecules have some charge separation characteristic of isolated molecules, the paradigm being benzyl chloride. Thus as discussed earlier,^{3,12,13} a concerted transition state such as structure I is more easily attained in solvents which are less interactive with or competitive for the cation. Structure I is also expected to be more important for X equal to the hard chloride rather than the softer bromide, as the results substantiate. It is possible, but most likely indeterminable, that the reactivity is doubly benefitted by both cation assistance due to $\text{R}^{\delta+}\text{-X}^{\delta-}\cdots\text{Na}^+$ formation as well as by directing the RX to a convenient position for M-R bond formation. An inversion of configuration at carbon is not a requirement for the model proposed. Neither is it assured that the initial bond-forming process should be that of $\text{M}-\alpha\text{-C}_{\text{carbanion ion}}$. That is, remote attack is possible with such charge-delocalized carbanion ions.

It might be argued that the same solvent environment that promotes $\text{M}-\text{CO}\cdots\text{Na}^+$ ion-pair formation also promotes $\text{R}^{\delta+}\text{-X}^{\delta-}\cdots\text{Na}^+$ interaction. Significantly, the addition of $\text{Na}^+\text{BPh}_4^-$ (ion-pair dissociation constant in THF = 8.5×10^{-5} M) in tenfold amounts to $\text{Na}^+\text{CpMo}(\text{CO})_3^-$ (ion-pair dissociation constant in THF = 4.1×10^{-6}) only slightly lowered the rate for $n\text{-BuI}$ addition (Table V) and did not affect the rate for $\text{BzI}Cl$ addition. As mentioned before, $\text{Na}^+\text{CpMo}(\text{CO})_3^-$ exists in the contact ion-pair form to the extent of 100% in pure THF; hence addition of $\text{Na}^+\text{BPh}_4^-$ neither significantly increases the amount of contact $\text{Na}^+\text{CpMo}(\text{CO})_3^-$ nor, evidently, does it itself provide cation assistance to RX bond cleavage. It appears that cation assistance in the form of both leaving group assistance and a structure formation conducive to M-R bond formation is important in the transition state.

The factors which influence the oxidative addition reaction have been quite well analyzed for neutral transition metal complexes.⁴⁸ That a larger number of mechanistic subtleties exist for anionic complexes is consistent with the myriad of solution structures possible. We have defined those structures for $\text{CpMo}(\text{CO})_3^-$ salts

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and have linked them to reaction patterns.

Acknowledgment. This work was supported by a grant from the National Science Foundation, No. CHE-79-23204. The authors also acknowledge the purchase of an inert-atmosphere drybox by the Research Corporation. Discussions with R. G. Bergman and D. J. Darensbourg were especially helpful.

Registry No. Li⁺CpMo(CO)₃⁻, 68550-41-4; Na⁺CpMo(CO)₃⁻, 12107-35-6; K⁺CpMo(CO)₃³⁻, 62866-01-7; PPN⁺CpMo(CO)₃⁻, 67486-18-4; Li⁺CpCr(CO)₃⁻, 48121-51-3; Na⁺CpCr(CO)₃⁻, 12203-12-2; K⁺CpCr(CO)₃⁻, 69661-90-1; Li⁺CpW(CO)₃⁻, 80662-55-1; Na⁺CpW(CO)₃⁻, 12107-36-7; K⁺CpW(CO)₃⁻, 62866-03-9; HMPA, 1608-26-0; *n*-BuI, 542-69-8; *n*-BuBr, 109-65-9; BzI, 100-44-7; BzIBr, 100-39-0; CpMo(CO)₃CH₂Ph, 12194-07-9.

Energy Surfaces in the Cyclopropane Radical Ion and the Photoelectron Spectrum of Cyclopropane

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Abstract: We have performed calculations to determine the two lowest energy surfaces of the cyclopropane radical cation. These are degenerate at a number of geometries, including, of course, arrangements with *D*_{3h} symmetry. We have used a method we call targeted correlation. This is a flexible procedure allowing us to tailor wave functions to a particular problem by treating the electron correlation in selected regions of a molecule accurately, while using more economical descriptions in other parts of the molecule. The lower surface shows a relatively flat pseudorotation region with three symmetrically equivalent saddle points of one type, three symmetrically equivalent saddle points of another type, and six symmetrically equivalent minima. The three-membered carbon ring is a scalene triangle at each of the minima. The total change in the energy along the pseudorotation path is approximately 0.3 eV. The upper surface does not show a pseudorotation region but has three relatively deep, symmetrically equivalent minima which correspond to an open-ring trimethylene radical ion isomer. Our calculations give a difference of 1.3 eV between the upper energy and the lower energy minima. When this result is combined with our calculated energy for neutral cyclopropane, we estimate 9.8 and 11.1 eV for the adiabatic onset positions of the first two peaks in the PES of cyclopropane. These compare very well with experiment. A more complex description of the PES peak profile is also offered.

Cyclopropane is a very important substance for theoretical study since it incorporates in one small molecule many physical and chemical phenomena and provides opportunities for intercomparisons. When represented by the Walsh model,¹ C₃H₆ has both Hückel and Möbius² orbital systems. It may also be considered the smallest aromatic system.³ C₃H₆ has also been studied by many experimental techniques. Among these is the photoelectron spectrum (PES), which has been determined for C₃H₆⁴ and many substituted versions.⁵ The understanding of the substituent effects on the PES depends on an understanding of the PES of the parent compound.

The several theoretical studies of C₃H₆⁺ have used semi-empirical methods and have attempted to determine the parameters of the surfaces from calculations restricted to C_{2v} geometries for which the C₃ triangle is always at least isosceles.⁶ The most involved analysis is that of Rowland who uses Koopmann's theorem and closed-shell CNDO calculations of the parent C₃H₆ to estimate functional dependence of the Jahn-Teller surfaces for the ion up to quadratic terms and then does a vibronic analysis to get the band profile. He finds a double-peaked distribution of vi-

brational intensities with a separation of 0.37 eV, a value three times too small.

In this article we describe the results of our ab initio calculations giving portions of the first two energy surfaces of C₃H₆⁺, the final state in the PES. We have extended the calculations to C_v geometries where the C₃ triangle is scalene. These results provide some new insight into the details of these energy surfaces relating them to various chemically interesting bonding patterns. We also discuss the relationship between these energy surfaces and the vibronic coupling which ultimately determines the vibrational structure of the ion and the profile of the PES peak.

Details of the Calculations

To obtain the C₃H₆⁺ energy surfaces we have used the method of *targeted correlation*⁷ which is described elsewhere. Since we are, in this case, principally interested in the dependence of the energy upon the geometry of the C₃ triangle, this provides a useful simplification by allowing a more accurate treatment of the correlation in the C-C bonds than in the C-H bonds. In line with this we consider no geometries in which the C-H distances are significantly distorted from the equilibrium value.

For C₃H₆⁺ we assemble the targeted correlation wave function from SCF orbitals for three separate methylene fragments. It is possible to orient CH₂ so that the ground state is ³B₂ in C_{2v} symmetry. The ground configuration is then (1a₁)²(2a₁)²(1b₁)²(3a₁)(1b₂), and we have determined these by a conventional open-shell Roothaan SCF procedure⁸ using 3G STOs⁹ as the AO basis. These orbitals were determined as a function of the H-C-H

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